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Emissions and Residue Values from Waste Disposal During Wood Preserving

Acurex Corp.
Mountain View, CA

Prepared for

Industrial Environmental Research Lab.
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By
Bruce DaRos, Richard Merrill, Dr. H. Kirk Willard and Dr. C. Dean Wolbach
Acurex Corporation
Energy & Environmental Division
Mountain View, California 94042

Contracts 68-03-2567 (Task 4028) and 68-03-3028 (Task 10)

For
Technical Project Monitor
Donald Wilson
Food and Wood Products Branch
Industrial Environmental Research Laboratory
Cincinnati, Ohio 45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
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This document reports emissions and residue that were measured from thermal (pan) evaporation, spray pond evaporation, and direct combustion of organic components in wood preserving wastewater. The information presented includes plant and evaporation device descriptions, test plans, sampling and analytical results, and conclusions and recommendations. Also presented are qualitative descriptions of the fugitive emissions and residues that occur during processing operations.

The primary conclusions are that organic compounds are emitted to the atmosphere during thermal (pan) evaporation. Organic emissions from the spray pond were below detectable levels. Contrarily, solid residues in evaporaters had low concentrations of toxic organic constituents while residues in spray ponds contained much higher levels than the feed wastewater. Fugitive organic emissions from the retort and vacuum vents were in high concentration although of limited duration. Thermal destruction of wastewater sludge by co-firing in an industrial wood fired boiler was 96 to 99.99+ percent complete for all organic components measured. Dioxins and furan values varied too much for removal determination but were evident in all ash and sludge samples. Details of their analysis by three laboratories are given.

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report documents several recently completed field investigations. Their purpose was to qualitatively and, when possible, quantitatively assess the organic emissions to air, water and land resulting from the evaporation and thermal destruction of wastewater generated by the wood preserving industry. Emphasis was placed on the toxic components emitted. The findings of this report can be used to quantify the practice and extent of organic constituents released to the environment. For further information, contact the Food and Wood Products Branch, IERL, Cincinnati, Ohio.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

Restriction of the discharge of wastewater generated during the preservation of wood has resulted in the increased use of evaporation techniques by the wood preserving industry. This report is the second phase of work described in EPA report 600/2-81-066 "Wood Preserving Industry Multimedia Emission Inventory." This document reports emissions and residue that were measured from thermal (pan) evaporation, spray pond evaporation, and direct combustion of organic components in the wastewater. The information presented includes plant and evaporation device descriptions, test plans, sampling and analytical results, and conclusions and recommendations. Also presented are qualitative descriptions of the fugitive emissions and residues that occur during processing operations.

It was concluded that toxic materials are both emitted and disposed of as residue. This included organic compounds (phenols and polynuclear aromatics) that were emitted to the atmosphere during thermal (pan) evaporation. Organic emissions from the spray pond were below detectable levels. Contrarily, solid residues from evaporators had low concentrations of toxic organic constituents while residues in spray ponds contained much higher levels than the feed wastewater. Fugitive organic emissions from the retort and vacuum vents were in high concentration although of limited duration. Thermal destruction of wastewater sludge by co-firing in an industrial wood fired boiler was 96 to 99.99+ percent complete for all organic components measured. Dioxine and furan values varied too much for removal determination but were evident in all ash and sludge samples.

This report was submitted in fulfillment of Contract 68-03-2567 Task 4028 and 68-03-3028 Task 10 under the sponsorship of the U.S. Environmental Protection Agency. Analysis by Wright State University, Monsanto Research and the University of Umea are included. This report covers a period from June 1980 to August 1981, and work was completed as of May 1981.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

EGD -- Effluent Guidelines Division (of EPA)
EPA -- Environmental Protection Agency
FWPCA -- Federal Water Pollution Control Act
GC/MS -- gas chromatography/mass spectrometry
IERL-Ci -- Industrial Environmental Research Laboratory, Cincinnati
μg -- microgram
kg -- kilogram
l -- liter
LP -- liquified petroleum
m -- meter
mg -- milligram
ng -- nanogram (10^{-9} gram)
NIOSH -- National Institute for Occupational Safety and Health
OPTS -- Office of Pesticides and Toxic Substances
OSW -- Office of Solid Waste
PAH -- polynuclear aromatic hydrocarbons
penta -- pentachlorophenol
POTW -- publicly owned treatment works
ppb -- parts per billion
ppm -- parts per million
RCRA -- Resource Conservation and Recovery Act
RPAR -- rebuttable presumption against registration
sm^3 -- standard cubic meter
CDF -- chlorodibenzofurans
CDD -- chlorodibenzodioxins
ND -- nondetectable

SYMBOLS

P_A = partial pressure of component A

P_A^o = partial pressure of pure component A at the temperature of the solution

X_A = mole fraction of component A in solution

R_i = rate of discharge of i^{th} stream

C_{ij} = concentration of j^{th} component in i^{th} stream

V_1 = volume of wastewater in evaporator (liters)

C_{AS} = saturation concentration of A (mg/l)

C_A = steady state concentration of A (mg/l)

V_g = volume of water evaporated (liter)

C_{Ag} = concentration of component A in emission (mg/l)

W_a = evaporation rate, gmole/sec

D = droplet diameter, cm

C_f = molar concentration of air, 3.88×10^{-5} gmole/cc

D_a = diffisivity, cm^2/sec

X_a = vapor pressure of the liquid

V_∞ = velocity of droplet (assume terminal velocity), cm/sec

ρ_f = density of air, 1.12×10^{-3} g/cc

M_f = viscosity of air

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SECTION 1

INTRODUCTION

The wood preserving industry consists of approximately 475 production plants owned by approximately 300 companies. The primary products of this industry are utility poles, railroad ties, and construction materials, chemically treated to resist insect and fungi attack, improve weathering characteristics, and promote insolubility in water and fire retardance. The preservatives used to produce the desired product characteristics include creosote, a coal tar derivative; pentachlorophenol, a crystalline compound dissolved in light aromatic oil; and waterborne salts of arsenic, chromium, copper, zinc, and fluoride.

The application of the preservatives requires certain processing steps. The wood must first be debarked, formed (cut to size and shaped as necessary), and conditioned. The conditioning step removes the water from the wood, increasing its permeability and ability to accept the preservatives. Drying the wood can be done by air seasoning, tunnel drying, or kiln drying, all independent of the preserving step. The wood may also be conditioned in combination with the preserving step as in steam conditioning, boultonizing, or vapor drying. Each of these latter processes generates a wastewater stream containing wood extracts and preservatives which must be disposed of.

The toxic nature of the preservatives used by the wood industry has led the Effluent Guidelines Division of the Environmental Protection Agency (EPA) to promulgate regulations governing the disposal of the generated wastewater.(1) The regulations presently in effect which do not allow the direct discharge of wastewater to receiving streams have led plant operators to develop disposal technologies other than direct discharge. The primary purpose of this report is to discuss the results of test programs conducted to quantify the uncontrolled transfer of toxic organic species contained in the wastewater to other media. Waterborne salts were not included in this study as those processes can be controlled for wastewater discharges without adding air emissions.

The wastewater treatment or disposal technologies developed by the industry include plant process modifications, improved oil/water separation, wastewater treatment, evaporation, and discharge to public owned treatment works (POTW). Evaporation includes thermal (pan) evaporation, cooling towers, spray ponds, and solar ponds. Under EPA contract 68-03-2584, an operating cooling tower was tested which showed a very low discharge of organics. In addition, the thermal (pan) evaporation technique was evaluated in the laboratory; this work showed a significant fraction of the organic compounds in the wastewater being discharged to the atmosphere. To verify the release of organics from thermal (pan) evaporators, this task was funded. Also included in this task was the field testing of a spray evaporation pond and examination of waste disposal in an industrial steam boiler.

Other sources of organic emissions, in addition to the evaporator discharge, include fugitive emissions such as the dense vapor plumes emitted as the pressure vessel is opened and wood charge removed, and emissions from the treated wood as it cools and the vacuum exhaust. Fugitive residues are quite common as process chemical spills and dripping from treated wood or equipment. Quantifying data describing the fugitive emissions is not easily found in the literature.

The scope of work included plant identification, plant surveys, and site selections. The program objectives were to qualitatively and quantitatively evaluate multimedia emissions from a thermal (pan) evaporation device (including fugitive emissions from the treatment system) -- plant A, a spray pond system--plant B, and an industrial boiler using the oil-laden wastewater as supplemental fuel--plant C.

Section 2 of this report presents the conclusions reached during the execution of this task, followed by the recommendations in Section 3. Section 4 discusses the wastewater evaporation options available to plant operators, as well as thermal destruction of the wastewater. Sections 5 through 7 discuss the results of the thermal (pan) evaporation, the spray evaporation, and the boiler disposal test programs, respectively. Section 8 cover data on dioxin and furan analysis and finally, Section 9 presents the fugitive emissions and residues assessment.

Three appendices, one for each test program, present details of the field sampling and analytical programs. Included in each appendix is the data collected in the field for that test program. Handwritten field notes are not included but as a separate package are available directly from EPA's Industrial Environmental Research Laboratory, 26 W. St. Clair St., Cincinnati, OH 45268 (513/684-4227).

SECTION 2

CONCLUSIONS

The results of this program confirmed previous bench-scale simulated tests in that the discharge of organic compounds during wastewater evaporation in thermal (pan) evaporators showed that the emissions were greater than usual predictive methods would indicate. The toxic organic content of waste charged to the evaporators was many times higher than reported in the literature. Spray pond emissions were such that the cryogenic sampling systems as used did not yield enough sample material to detect the low volatility components of the wastewater if present. Therefore, of the evaporation systems studied, thermal (pan) evaporation had the most organic emissions and evaporators the least. Contrarily, solid residues in evaporators had low concentrations of toxic organic constituents while residues in spray ponds contained much higher levels than the feed wastewater.

The destruction of the organic compounds in an industrial steam boiler is a viable disposal option when the boiler is operated properly. The system tested accomplished a 96.1 to 99.99+ percent destruction efficiency for the phenols and PNAs measured. Certain chlorinated dioxins and furans were detected in the preserving waste feed and accumulated in the ash streams. The quantity of chlorinated dioxins and furans in flyash and bottom ash is higher than usually reported in the literature and includes fractions rarely measured from combustion. The most toxic isomer was not found in significant quantity but levels of dioxin in flyash were very high.

Industrywide, the air emissions from onsite treatment of wastewater handling had been estimated at <100 metric tons/year based on the reported mass of volatile organic compounds contained in wastewater requiring treatment. However, PNAs and other aromatic compounds were emitted at rates up to 12 kg/hr for the plant tested (which uses two thermal evaporators). The wide variation in pollutant releases (<2 to 11,300 g/hr and ~0 to 52,000 ppm) within one day or less for individual sources precludes establishing exact mass emissions. Measured fugitive emissions, although of high concentration, apparently were of relatively short duration. Thus, although localized emissions do occur, the industry in total is not as large of an emitter of organics as some other industry segments. Table 1 presents a summary of the organic emissions discharged from the evaporation devices.

Solid residues produced from each process must be recycled back to the process for reuse or disposed in a manner cognizant of the toxic components identified and quantified.

TABLE 1. SUMMARY OF EMISSIONS AND RESIDUES OF ORGANIC COMPOUNDS*

Source	Emission concentration (ppm or μg/g)	Emissions rate g/hr	Residues concentration μg/g
Thermal evaporator	36 to 1,500	1.8 to 11,300	75
Spray pond evaporation	<1	--	48,000
Retort emissions/residues	220 to 3,700	--	2,100 to 14,000
Vacuum vent emissions	22,000 to 52,000	0 to 20,000	

*Organic constituents include volatile and semivolatile (PNAs) compounds only. Residues include only separately wasted material, not recycled streams.

SECTION 3

RECOMMENDATIONS

If evaporation technology is to be employed, it must be recognized that the thermal (pan) evaporation system is an emitter of organic components to the atmosphere and its minimal use, if it is used, would lessen air emittants.

Regardless of the evaporator used, care should be taken to develop oil/water separation techniques which minimize oil and sludge carryover to the evaporator. A program should be conducted to establish the best available separation systems or to develop methods to enhance the operation of existing systems. Systems with potential applicability include chemical flocculation, solvent extraction, biological pretreatment, and land application. A preliminary study funded by IERL-Ci (EPA-600/2-81-043, 1981) has covered part of the first three mentioned treatments. Disposal of residue from systems that minimized air emissions must be accomplished by modes (preferrably by reuse) that do not adversely impact the land.

The destruction of wood preserving wastes by co-firing in boilers can be accomplished with minimal environmental impacts. It is recommended that industry pursue such disposal. Also a program should be conducted to determine the proper injection (atomization) methods, and the residence times and temperatures necessary to satisfactorily destroy the organics in the waste at higher loadings. Such an incineration study could productively be extended to include the ash and a variety of sludges. Further analysis of the most toxic byproducts (possibly furans) should be extended for better speciation and quantification of the chlorinated dibenzo-p-dioxins and chlorinated dibenzofurans. Careful evaluation should be conducted of the partitioning of these organic components in ash, especially where no baghouse is used.

Fugitive emission and residue studies should be extended to include the duration of emission or flowrates and extent of on-site land (or subsoil) contamination. Such information could be utilized along with the existing concentration values to quantify these pollutant sources.

If further testing of very low level emissions from ponds are undertaken it is recommended that surface emissions be sampled separately from spray drift sampling. Surface emissions can be analyzed from samples of the air layer above the surface. That air layer would contain all pollutants emitted if the surface is enclosed by a bubble film that excludes all surrounding air transfer. Particle or aerosol drift can be better sampled by a high volume collection device.

SECTION 4

WASTEWATER TREATMENT AND DISPOSAL BY ALTERNATIVES TO DIRECT DISCHARGE

The treatment of wood with preservatives requires impregnation of the wood with toxic materials designed to protect it from attack by insects, fungi, weather, or fire. The processing steps include wood preparation (debarking, shaping, drying) and preservative application. The preservative can be applied using either pressure or nonpressure techniques. Nonpressure techniques are used when only minimal treatment is necessary. Pressure processes require the use of pressure or vacuum steps, either for preservative application or for combinations of wood conditioning (to increase permeability) and preservative application. Wood conditioning processes generate steam (due to the water content of the wood and the pressure/temperature/vacuum operations) which contains wood extractives and organic constituents from the preservative formulation. The heat content of the steam volatilizes low-molecular-weight organic compounds such as benzene and toluene, or atomizes drops of emulsified preservative, carrier oil, and water. When the resulting vapors are removed from the retort and condensed, the condensate contains water, free oils (and preservatives), emulsified oils (and preservatives), and wood extractives. Following removal of the free oils, the wastewater stream is transported to a disposal facility.

Industry's technical response to requirements for process wastewater control has included increased evaporation of water using thermal (pan) evaporators, spray and solar ponds, and cooling towers to decrease aqueous discharges. The principle behind the evaporation of the wastewater is to dispose of the water fraction while leaving the organic constituent for subsequent recycling to the process or landfill disposal. Since volatile and other low-molecular-weight organic constituents are present in the wastewater, they may be released to the atmosphere. This section briefly reviews the rules impacting wastewater discharge and describes each of the above mentioned evaporation devices and their emissions.

4.1 FEDERAL REGULATIONS IMPACTING/PRESERVING INDUSTRY EMISSIONS

The purpose of the wood preserving industry, to turn wood, a nutritious food source for microorganisms and insects, into an unpalatable nondecaying material, involves toxic material by nature. Thus regulatory agency concern for process losses and discharges has been active for many years. In the following paragraphs the recent federal rules that impact this industry's emissions have been briefly reviewed. The impact of promulgating rules covering ongoing industry practices is generally to thrust the regulated practice toward an economical control or option. Rules currently in force are effecting an alternative to direct discharge.

For the wood preserving industry, EPA has promulgated regulations for Best Practicable Control Technology (BPT), Best Available Technology Economically Achievable (BATEA), Best Conventional Pollutant Control Technology (BCT), New Source Performance Standards (NSPS), Pretreatment Standards for New Sources (PSNS), and Pretreatment Standards for Existing Sources (PSES), under authority of sections 301, 304, 306, 307, and 501 of The Clean Water Act of 1977.(1)

For the waterborne or nonpressure subcategory of the wood preserving industry, BPT, BAT, and NSPS are defined as allowing no discharge of process wastewater pollutants. For indirect dischargers, PSES and PSNS allow no introduction of process wastewater pollutants. The Boulton subcategory is subject to the same discharge limitations for BPT, BAT, NSPS and PSNS, although pretreatment standards to the existing sources limit oil and grease (O&G) to a maximum of 100 mg/l for any one day and pentachlorophenol to 0 mg/l. This is equivalent to 20.5 g/m^3 of production for oil and grease where POTWs impose mass limitation. The steam subcategory has a no-discharge limitation for NSPS and PSNS while PSES is the same as for the Boulton subcategory. BPT for this subcategory limits COD, phenol and O&G discharges.

An exclusion exists under the implementation of the Resource Conservation and Recovery Act of 1976 for waste oils and solvents. By rules established in the Federal Register, May 19, 1980, the burning of hazardous waste for energy recovery was excluded under the hazardous waste provision of RCRA. Thus, burning waste oils and solvents in a boiler to provide steam or usable energy is not covered under RCRA Subtitle C although storage or transportation of a listed hazardous waste prior to burning is covered.

Hazardous wastes that are reused, recycled or reclaimed are also excluded from most requirements under subtitle C of RCRA, although they are still subject to regulations regarding transportation and storage.

Under section 3001 of RCRA, bottom sediment sludge from the treatment of wastewaters from wood preserving processes, that use creosote or pentachlorophenol is considered a hazardous waste because of toxicity. The release of more than one pound of this sludge may be a reportable event under sections 103 (a) and (b) of Superfund (Comprehensive Environmental Response, Compensation and Liability Act of 1980).

Under section 112 of the Clean Air Act, EPA has listed seven pollutant species as hazardous air pollutants and is currently developing National Emissions Standards for Hazardous Air Pollutants (NESHAPS) for sources. In addition, several other species are under consideration for listing and possible NESHAPS development. Of the seven listed hazardous air pollutants (mercury, benzene, radionuclides, asbestos, vinyl chloride, beryllium and arsenic), none apply specifically to the wood preserving industry. Although benzene emissions have been found, the regulations only concern benzene from maleic anhydride manufacture. Candidate species for NESHAPS consideration which are of possible concern to the wood preserving industry include phenol and toluene.

Acting under the authority of the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA), EPA published notice on October 18, 1978, of rebuttable presumption against regulation (RPAR) and continued registration of pesticide products containing pentachlorophenol and its derivatives, as well as inorganic arsenic, creosote, coal tar and derivatives. The notice served merely to request information on the risks and benefits associated with these pesticides. Later in the year, the Science Advisory Board produced a report on pentachlorophenol contaminants, which addressed the question of whether polychlorinated dibenzodioxins present in penta contributed to increased health hazards as a result of penta use.

On February 19, 1981 (40 FR 13020) EPA published a Notice of Determination concluding the RPAR investigations. Although preliminary the Agency "concluded that the available information is still insufficient" for determining toxic effects. EPA determined that the preservatives continue to exceed risk criteria (40 CFR 162.11) and risks "are greater than the social, economic, and environmental benefits" of existing use unless risk can be reduced by registration changes. Some changes will be effected in the near future such as restricting penta spray applications.

4.2 SURFACE EVAPORATION EMISSIONS

While evaporative processes allow plant operators to dispose of wastewater but with zero direct discharge, they are operated under the assumption that insignificant organic compounds are transferred to the air. With EPA IERL-Ci funding, a prior program was conducted to determine if organic compounds were emitted to the atmosphere.(2) The primary results of that program indicated that organic components of the wastewater were discharged during evaporation.

The mathematical expression for the evaporation rate of chlorinated phenolic and other organic chemical pollutants from the surface of wastewater evaporation systems (thermal evaporation ponds or pan evaporators) can be developed from Fick's first law of diffusion. The following qualifying assumptions must be made:

- The system is at steady state (i.e., the liquid is at equilibrium with the gas at the liquid surface)
- The wastewater is an ideal solution
- There is a stagnant layer of air above the pond
- The vaporized organic compound forms an ideal gas mixture with air
- The solubility of air in the wastewater is negligible
- There is constant temperature and pressure in the stagnant air layer

With these assumptions, the minimum evaporation rate of each organic pollutant in the wastewater can be estimated using equation 1. This equation is expressed in terms of total and partial pressures:

$$N_A \Big|_{z=z_1} = \frac{P_T D_{AB}/RT}{(z_2 - z_1)} \cdot \ln\left(\frac{P_T - P_{A_{Z2}}}{P_T - P_{A_{Z1}}}\right) \qquad (1)$$

where:

N_A = molar flux of species A into B in the z direction, gmoles $L^{-2}t^{-1}$
P_T = total pressure, atm
D_{AB} = binary diffusivity for system composed of species A and B, L^2t^{-1}
P_{A_Z} = partial pressure of species A, atm
R = gas constant, 82.05 cm^3 atm $gmole^{-1}\,{}^oK^{-1}$
T = ambient air temperature, ^oK
z_2-z_1 = film thickness, cm

This expression shows the diffusivity and partial pressures impact on the rate of organic emissions: as temperature increases, the diffusivity increases. Therefore, higher-molecular-weight compounds can be driven out of solution.

In estimating the evaporation rate of organic vapors into air, it is assumed that the diffusion layer (z_2-z_1) is finite, that the air is stagnant and insoluble in the organic compound within that layer, and that the contained wastewater surface is quiescent. Therefore, if the air above the surface is turbulent, z_2-z_1 approaches zero, maximizing the transfer rate of the organics to the atmosphere.

The diffusivity and vapor pressures calculated from these equations can be used in estimating the evaporation rate of a pure organic liquid into air if the organic constituents formed a layer over the wastewater. To estimate the evaporation rate of an organic liquid from an aqueous solution (emulsion), it is assumed that the organic compound forms an ideal solution with water and that its vapor forms an ideal mixture in air. The evaporation rate of the organic from the solution is given by the product of the pure liquid evaporation rate and the mole fraction of organic in the wastewater.

It has been demonstrated in the laboratory and field that organic material is stripped from water solutions.(3,4) The transfer of chlorinated organics from water solutions to the atmosphere is controlled by their rate of diffusion and concentration in water and the thermal driving force.

This evaporation model is applicable to solar ponds and thermal (pan) evaporators. A solar pond is a contained area where the wastewater is placed and allowed to evaporate. The pond may be lined or unlined. An unlined pond depends on soil attenuation to prevent organic materials from entering exceeds the annual precipitation rate for a given geographical area. Solar ponds require large land area, and federal regulations now require that ponds containing hazardous materials must meet berm maintenance requirements and use monitoring wells for leachate control. The cost of complying with these regulations may cause plant operators to install other evaporation technology.

The evaporation process can be accelerated by applying heat directly to evaporate the water, as in a thermal (pan) evaporator. In this system, the wastewater is contained in a vessel, such as a tank or lined pond, which is heated by an external source, such as boiler steam or the condenser system. The wastewater can be used as a cooling fluid to condense the vapor from the retort then recycle back to the evaporation system. As the temperature is increased, wastewater and organic materials are emitted.

4.3 DROPLET EVAPORATION IN SPRAY PONDS AND COOLING TOWERS

Another mechanism for enhancing evaporation is the formation of droplets. This method creates large liquid surface areas, promoting greater liquid/air contact and accelerated evaporation rates.

The evaporation rate of organic compounds from a droplet of wastewater can be estimated using an equation for the evaporation rate of a free-falling drop. Assuming that the evaporation rate is sufficiently small not to distort the velocity and concentration profiles, and that the mass transfer coefficient is independent of mass transfer rate, the resulting equation for predicting the evaporation rate is shown below:

$$W_a = \frac{\pi D C_f D_a}{4} \cdot \frac{x_{a_o} - x_{a_\infty}}{1 - x_{a_o}} \left[2.0 + 0.60 \left(\frac{D V_\infty \rho_f}{M_f} \right)^{1/2} \left(\frac{M}{D} \right)_f^{1/3} \right]$$

where:

W_a = evaporation rate, gmole/sec
D = droplet diameter, cm
C_f = molar concentration of air, 3.88×10^{-5} gmole/cc
D_a = diffusivity, cm^2/sec
X_a = vapor pressure of the liquid
V = velocity of droplet (assume terminal velocity), cm/sec
ρ_f = density of air, 1.12×10^{-3} g/cc
M_f = viscosity of air

This evaporation system again is impacted by diffusivity and partial pressure; air resistance also affects the rate of evaporation.

This evaporation model is applicable to spray pond systems and cooling towers. A spray pond is a contained area (lined or unlined pond) which has a pumping system connected to spray nozzles. This system decreases both the land required by a solar pond and the effect of negative climatic impacts.

The use of a cooling tower is applicable specifically to Boulton conditioning systems. As the water vapor from the retort is condensed, it gives up heat. The condensed wastewater is accumulated, then sent to the oil/water separator. The effluent wastewater from the oil/water separator is added to the cooling water that recirculates through the condenser and sent through the cooling tower. The waste heat promotes evaporation. In steaming plants, there is insufficient waste heat to evaporate the volume of wastewater generated.

A field test program was conducted at a site utilizing a cooling tower to measure the presence of organic compounds in the air stream. It was found that low-molecular-weight compounds were emitted to the atmosphere but that volatile organics remained in solution.(2) This reafirmed an earlier EPA funded study on a cooling tower at a forest products plant.(5)

Other evaporation processes are also used by the wood preserving industry. In land irrigation, the wastewater is sprayed or flooded onto a field. In the case of spraying, wastewater droplet evaporation occurs followed by solar evaporation of the ponded waste. Subsequently, water percolates into the soil.

4.4 OTHER ENVIRONMENTAL IMPACTS: FUGITIVE AND RESIDUE LOADS

Each of the wastewater treatment processes described produces a residual sludge. The amount of solid waste material generated depends on the preservative used, and the effectiveness of the oil/water separator and the treatment technologies employed. This material is typically disposed in landfills (usually onsite if land is available). Incineration of solid waste is a very limited practice at preserving plants.

Other sources of organic emissions, in addition to the evaporator discharge, include fugitive emissions such as the dense vapor plumes emitted as the pressure vessel is opened and wood charge removed, and emissions from the treated wood as it cools and the vacuum exhaust. Fugitive residues are quite common as process chemical spills and dripping from treated wood or equipment. Quantifying data describing the fugitive emissions is not easily found in the literature. A primary purpose of this program was to collect additional field data to further evaluate the multimedia impacts occuring during wastewater disposal onsite for the wood preserving industry.

SECTION 5

CHARACTERIZATION OF MULTIMEDIA EMISSIONS FROM A THERMAL (PAN) EVAPORATION DEVICE

A field test program was conducted at a wood preserving plant (plant A) which used thermal (pan) evaporation to reduce its generated wastewater volume. The program was designed to determine the organic emissions and residues from two thermal (pan) evaporators, one evaporating wastewater containing penta and other chlorinated phenolic compounds, and one evaporating wastewater containing creosote components including polynuclear aromatic hydrocarbons (PAHs). Each system stream was qualitatively and semiquantitatively analyzed for organic compounds, including chlorinated phenols, chlorinated dibenzo-p-dioxins, chlorinated dibenzofurans, and PAHs.

5.1 PROGRAM DESCRIPTION AND RESULTS

This program focused on the primary multimedia effluents generated by the plant which were expected to represent the greatest environmental impacts in terms of gaseous and solid discharges. No wastewater discharge from plant boundaries is permitted by law. The sampling points of interest were the ducted and fugitive air emissions, and solid wastes from housecleaning and wastewater treatment. Because of the batch nature of the preserving process and the variability of the input materials (wood), the cost of a program extensive enough to generate a meaningful plantwide material balance was determined to be prohibitive. In addition, the primary focus was environmental impacts. Material measurements were conducted at each evaporator since they represented the only processes which were totally quantifiable processes, and the evaporators were expected to generate a majority of the air and solid emissons. A primary objective of this program was to quantify the emission rate of specific organic compounds from the evaporation devices.

5.1.1 Test Site

The wood treating facility selected for field testing employed two treating cylinders using the Boulton conditioning process. One cylinder could treat wood with penta formulations, while the other cylinder could treat wood with either penta or creosote.

Condensate generated from the individual treating processes was handled by discrete subsurface oil/water separators on a batch basis. The recovered oil fraction was returned to bulk storage tanks for reuse in the process.

Separated sludges and wastewater were routed to the appropriate thermal (pan) evaporators — one penta and one creosote — for volume reduction. Figure 1 presents a schematic of the plant wastewater/preservative recovery system.

Each evaporator was operated on a semibatch basis. As the wastewaters were transferred to their respective evaporators, steam from the boilers was pumped through steam coils in the tanks to heat the wastewaters to boiling, driving off the water. This process was continued until an oil/preservative layer accumulated which was returned to the preservative work tanks. Semiannually the evaporators were opened, and the nonpumpable sludge layer removed. Sludge generation is approximately 34 metric tons/year/evaporator, and is disposed of in 55-gal (208 l) drums which are hauled to a landfill.

5.1.2 Field Test Program

The sampling program conducted included each of these tests:

- Source emission sampling at the penta and creosote thermal (pan) evaporator outlets
- Total hydrocarbon determinations at each air emission point
- Specific low-molecular-weight hydrocarbon determinations at each emission point
- Grab samples of:
    - Penta thermal (pan) evaporator contents
    - Creosote thermal (pan) evaporator contents
    - Bulk penta in treating oil
    - Bulk creosote treating material
    - Penta oil/water separator (both fractions)
    - Creosote oil/water separator (both fractions)

The sample collection matrix is shown in Table 2. A schematic of the process, showing sample locations, is presented in Figure 2. Source emissions sampling was conducted using the EPA Method 5 sampling train with XAD-2 resins for nonvolatile organic compounds. Volatile organic emissions were measured using field gas chromatography (GC) techniques. Samples of the liquid fractions were randomly collected by grab sampling during each test series. A complete discussion of the field testing and the test data are contained in Appendix A.

5.1.3 Data Presentation for Pan Evaporation

The measured pollutant concentration data for the pan evaporator tests are given in Tables 3 to 8. Average values for the penta pan evaporator tests

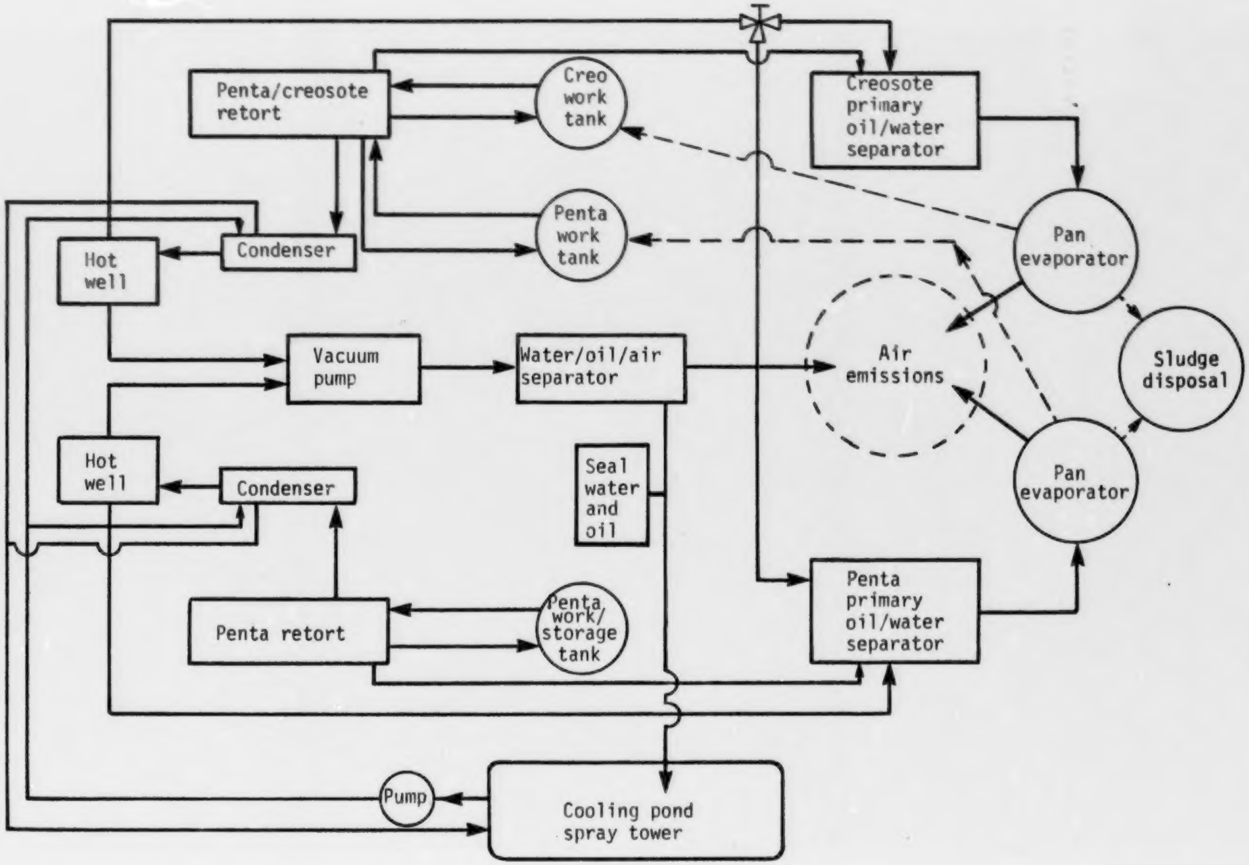

Penta/creosote retort
Creo work tank
Creosote primary oil/water separator
Condenser
Hot well
Penta work tank
Pan evaporator
Vacuum pump
Water/oil/air separator
Air emissions
Sludge disposal
Hot well
Condenser
Seal water and oil
Pan evaporator
Penta retort
Penta work/storage tank
Penta primary oil/water separator
Pump
Cooling pond spray tower

Figure 1. Schematic of wood preserving plant wastewater/preservative recovery system.

TABLE 2. SUMMARY OF COLLECTED SAMPLES*

Sample location description Collection method	Penta** oil/ water separator	Creosote oil/ water separator	Penta evaporator	Creosote evaporator
Day 1 (Setup)				
Day 2				
XAD-2 air sample			X	X
Field GC			X	X (2)***
Liquid grab sample	X/X	X/X	X (2)	X (2)
Solid grab sample				
Day 3				
XAD-2			X	X
Field GC			X (2)	X (2)
Liquid grab sample	X/X		X	X
Solid grab sample			X	X
Day 4				
XAD-2			X	X
Field GC				
Liquid grab sample	X/X	X/X	X	X
Solid grab sample				

***(2) are for duplicates

**Oil layer and water layer measured separately

*Other sample locations were grab sampled

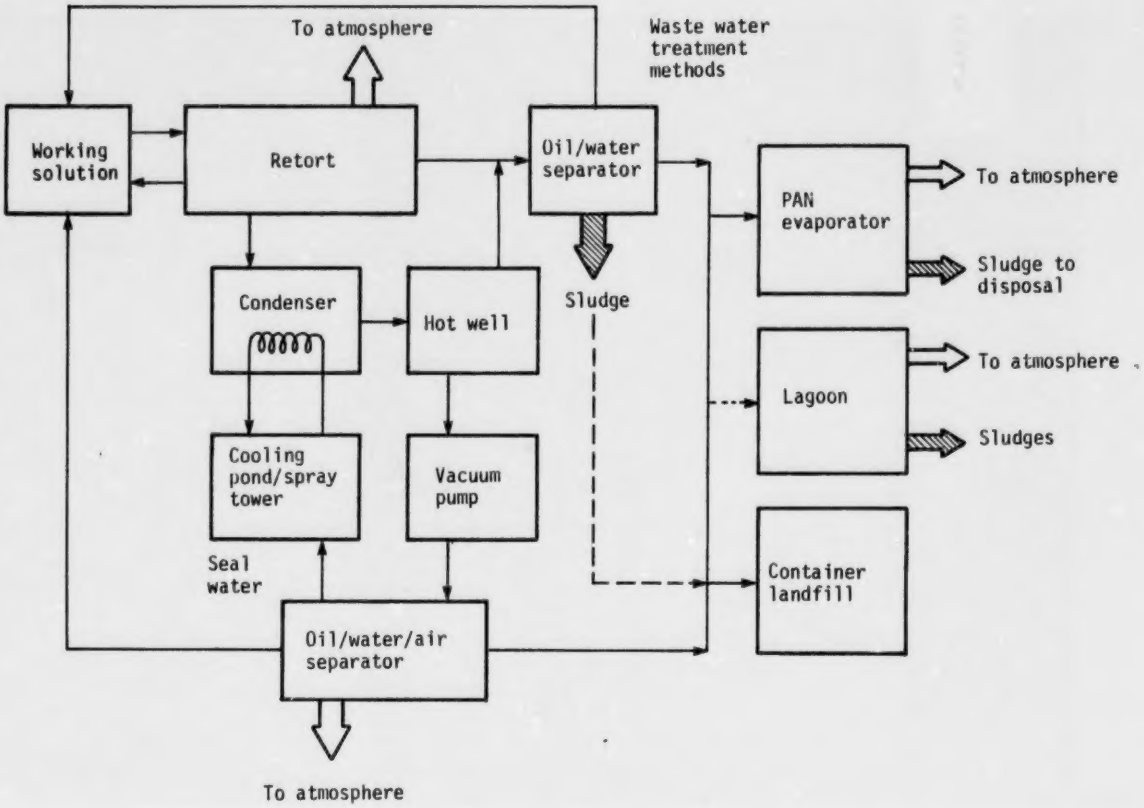

To atmosphere
Waste water treatment methods
Working solution
Retort
Oil/water separator
PAN evaporator
To atmosphere
Sludge to disposal
Sludge
Condenser
Hot well
Lagoon
To atmosphere
Sludges
Cooling pond/spray tower
Vacuum pump
Container landfill
Seal water
Oil/water/air separator
To atmosphere

Figure 2. Sampling locations for thermal (pan) evaporator tests and fugitive emissions tests.

TABLE 3. PENTA PAN EVAPORATOR — TEST 2

Stream	Working solution	Oil/water recycle	Waste-water	Pan water	Pan sludge	Pan vent
Date	9/23	9/24	9/24	9/24	9/23	9/24
Time	—	1300	1245	0900	—	1200
Concentration*	µg/ml	µg/ml	µg/ml	µg/ml	µg/g	mg/sm^3
Penta	44,000	40,000	14,000	140	62	1.8
Phenol	<200	<10	<10	0.5	1.2	<0.5
Fluoranthene	430	3,800	970	7.9	2.0	1.0
Naphthalene	3,800	3,700	1,500	0.4	1.1	2.0
Benzo(a)anthracene	<100	540	200	3.7	0.5	0.11
Benzo(a)pyrene	<100	110	40	0.1	0.05	<0.1
Benzofluoranthenes	<100	380	110	0.1	0.2	<0.1
Chrysene	<100	520	180	3.7	0.4	0.10
Acenaphthylene	170	140	310	0.1	0.05	<0.1
Anthracene	230	400	180	1.2	0.5	0.17
Benzo(g,h,i)perylene	<200	30	<10	<0.1	0.1	<0.1
Fluorene	1,100	2,700	850	1.4	1.0	<0.1
Phenanthrene	1,700	5,000	1,800	9.5	3.5	1.0
Dibenzo(a,h) anthracene	<200	4	<10	<0.1	0.1	<0.5
Indeno(1,2,3-c,d) pyrene	<200	15	<10	<0.1	0.1	<0.5
Pyrene	350	3,500	710	6.1	1.4	0.8
Benzene	<1	0.3	<10	<0.1	0.2	NA
Toluene	18	27	<10	<0.1	0.3	NA
Ethylbenzene	23	19	<10	<0.1	0.2	NA

*Concentration units are ppm w/w for solids, and liquids, and at 23°C, 1 atm for gases

TABLE 4. PENTA PAN EVAPORATOR — TEST 3

Stream	Working solution	Oil/water recycle	Waste-water	Pan water	Pan sludge	Pan vent
Date	9/23	9/25	9/25	9/25	9/23	9/25
Time	—	1500	1510	—	—	0800
Concentration*	μg/ml	μg/ml	μg/ml	μg/ml	μg/g	mg/sm^3
Penta	44,000	45,000	980	70	62	3.4
Phenol	<200	<10	<10	0.4	1.2	0.65
Fluoranthene	430	2,800	2,000	2.7	2.0	5.2
Naphthalene	3,800	2,000	220	0.1	1.1	3.0
Benzo(a)anthracene	<100	430	290	1.4	0.5	0.29
Benzo(a)pyrene	<100	96	68	<0.1	0.05	<0.1
Benzofluoranthenes	<100	320	190	<0.1	0.2	<0.1
Chrysene	<100	400	420	1.0	0.4	0.26
Acenaphthylene	170	370	1,600	0.3	0.05	1.3
Anthracene	230	1,100	400	0.4	0.5	2.3
Benzo(g,h,i)perylene	<200	7	<20	<0.1	<0.1	<0.1
Fluorene	1,100	2,400	2,100	2.6	1.0	3.1
Phenanthrene	1,700	4,000	3,600	2.4	3.5	9.2
Dibenzo(a,h)anthracene	<200	<10	<20	<0.1	<0.1	<0.1
Indeno(1,2,3-c,d)pyrene	<200	28	<20	<0.1	<0.1	<0.1
Pyrene	350	1,900	1,300	2.0	1.4	3.2
Benzene	<1	1.2	0.2	<0.2	<0.2	
Toluene	18	77	0.1	<0.2	0.3	
Ethylbenzene	23	2.3	1.2	<0.2	<0.2	

*Concentration units are ppm w/w for solids and liquids, and at 23°C, 1 atm for gases

TABLE 5. PENTA PAN EVAPORATOR -- TEST 4

Stream	Working solution	Oil/water recycle	Waste-water	Pan water	Pan sludge	Pan vent
Date	9/23	9/25	9/25	9/26	9/23	9/26
Time	--	1500	1510	--	--	1135
Concentration*	µg/ml	µg/ml	µg/ml	µg/ml	µg/g	mg/sm^3
Penta	44,000	45,000	980	41	62	30
Phenol	<200	<10	<10	0.3	1.2	0.52
Fluoranthene	430	2,800	2,000	1.2	2.0	1.7
Naphthalene	3,800	2,000	220	0.3	1.1	5.8
Benzo(a)anthracene	<100	430	290	0.9	0.5	0.20
Benzo(a)pyrene	<100	96	68	<0.1	0.05	$<5x10^{-3}$
Benzofluoranthenes	<100	320	190	<0.1	0.2	0.043
Chrysene	<100	400	420	0.7	0.4	0.190
Acenaphthylene	170	370	1,600	0.1	0.05	1.370
Anthracene	230	1,100	400	0.2	0.5	0.740
Benzo(g,h,i)perylene	<200	7	<20	<0.1	<0.1	$<5x10^{-3}$
Fluorene	1,100	2,400	2,100	1.7	1.0	1.7
Phenanthrene	1,700	4,000	3,600	1.5	3.5	1.5
Dibenzo(a,h)anthracene	<200	<10	<20	<0.1	<0.1	$<5x10^{-3}$
Indeno(1,2,3-c,d)pyrene	<200	28	<20	<0.1	<0.1	$<5x10^{-3}$
Pyrene	350	1,900	1,300	0.9	1.4	1.4
Benzene	<1	1.2	0.2	<0.2	<0.2	
Toluene	18	77	0.1	0.2	0.3	
Ethylbenzene	23	2.3	1.2	0.2	<0.2	

*Concentration units are ppm w/w for solids and liquids, and g/sm^3 (not mg/sm^3) at 23^{o}C, 1 atm for gases

TABLE 6. CREOSOTE PAN EVAPORATOR -- TEST 2

Stream	Working solution	Oil/water recycle	Waste-water	Pan water	Pan sludge	Pan vent
Date	9/23	9/24	9/24	9/24	9/23	9/24
Time	--	--	--	0830	--	1450
Concentration*	µg/ml	µg/ml	µg/ml	µg/ml	µg/g	mg/sm^3
Penta	17,000	3,600	12	3.4	260	<0.15
Phenol	400	1,500	7	11	30	15
Fluoranthene	32,000	33,000	20	20	590	25
Naphthalene	24,000	33,000	42	13	680	200
Benzo(a)anthracene	20,000	23,000	10	14	390	0.4
Benzo(a)pyrene	600	610	2	24	91	<0.05
Benzofluoranthenes	650	530	4	5.7	190	0.05
Chrysene	15,000	19,000	10	8.9	240	0.3
Acenaphthylene	5,700	3,400	2	1.2	840	7
Anthracene	12,000	69,000	7	9.9	260	32
Benzo(g,h,i)perylene	<500	<500	0.2	0.6	10	<0.05
Fluorene	36,000	38,000	16	2.5	660	110
Phenanthrene	37,000	41,000	19	3.2	1100	98
Dibenzo(a,h)anthracene	<500	<500	0.2	0.9	<10	<0.05
Indeno(1,2,3-c,d)pyrene	<500	<500	0.3	0.7	16	<0.05
Pyrene	27,000	27,000	15	16	440	16
Benzene	26	<50	<0.1	<0.1	6.7	
Toluene	2.7	<50	<0.1	<0.1	1.4	
Ethylbenzene	<0.5	<50	<0.1	<0.1	0.3	

*Concentration units are ppm w/w for solids and liquids, and at 23°C, 1 atm for gases

TABLE 7. CREOSOTE PAN EVAPORATOR — TEST 3

Stream	Working solution	Oil/water recycle	Waste-water	Pan water	Pan sludge	Pan vent
Date	9/23	9/25	9/25	9/25	9/23	9/25
Time	—	—	—	—	—	1005
Concentration*	μg/ml	μg/ml	μg/ml	μg/ml	μg/g	mg/sm^3
Penta	17,000	1,300	8.3	7.6	260	2.7
Phenol	400	800	5.2	31	30	58
Fluoranthene	32,000	13,000	140	9.3	590	20
Naphthalene	24,000	38,000	200	10	680	2,700
Benzo(a)anthracene	20,000	9,200	60	4.5	390	1.4
Benzo(a)pyrene	600	3,000	6.1	0.6	91	0.2
Benzofluoranthenes	650	500	15	1.4	190	0.7
Chrysene	15,000	5,400	50	3.7	240	1.2
Acenaphthylene	5,700	5,700	6	0.3	840	29
Anthracene	12,000	8,000	56	2.8	260	68
Benzo(g,h,i)perylene	<500	730	<10	<0.1	10	<0.05
Fluorene	36,000	35,000	110	8.9	660	550
Phenanthrene	37,000	22,000	190	15	1100	200
Dibenzo(a,h)anthracene	<500	1,500	<10	<0.1	<10	<0.05
Indeno(1,2,3-c,d)pyrene	<500	1,300	<10	0.1	16	<0.05
Pyrene	27,000	10,000	100	6.7	440	13
Benzene	26	27	<0.1	<0.1	6.7	
Toluene	2.7	0.5	<0.1	<0.1	1.4	
Ethylbenzene	<0.5	6.8	<0.1	<0.1	0.3	

*Concentration units are ppm w/w for solids and liquids, and at 23°C, 1 atm for gases

TABLE 8. CREOSOTE PAN EVAPORATOR -- TEST 4

Stream	Working solution	Oil/water recycle	Waste-water	Pan water	Pan sludge	Pan vent
Date	9/23	9/25	9/25	9/25	9/23	9/25
Time	--	--	--	--	--	1300
Concentration*	μg/ml	μg/ml	μg/ml	μg/ml	μg/g	mg/sm^3
Penta	17,000	1,300	8.3	0.5	260	1.6
Phenol	400	800	5.2	35	30	<0.05
Fluoranthene	32,000	13,000	140	6.0	590	21
Naphthalene	24,000	38,000	200	6.4	680	2,200
Benzo(a)anthracene	20,000	9,200	60	2.4	390	1.2
Benzo(a)pyrene	600	3,000	6.1	0.4	91	0.3
Benzofluoranthenes	650	500	15	0.8	190	1.3
Chrysene	15,000	5,400	50	1.9	240	0.9
Acenaphthylene	5,700	5,700	6	0.2	840	44
Anthracene	12,000	8,000	56	1.4	260	44
Benzo(g,h,i)perylene	<500	730	<10	<0.1	10	<0.05
Fluorene	36,000	35,000	110	6.0	660	580
Phenanthrene	37,000	22,000	190	12	1100	260
Dibenzo(a,h)anthracene	<500	1,500	<10	<0.1	<10	<0.05
Indeno(1,2,3-c,d)pyrene	<500	1,300	<10	<0.1	16	<0.05
Pyrene	27,000	10,000	100	4.2	440	16
Benzene	26	27	<0.1	3.4	6.7	
Toluene	2.7	0.5	<0.1	<0.2	1.4	
Ethylbenzene	<0.5	6.8	<0.1	0.3	0.3	

*Concentration units are ppm w/w for solids and liquids, and at 23°C, 1 atm for gases

and the creosote pan evaporator tests are shown in Tables 9 and 10, respectively. Note that in test 4 on the penta evaporator, the units of emission are in g/sm^3 (grams per standard cubic meter), rather than mg/sm^3 as for all other tests.

Concentrations of evaporator gaseous emissions are calculated by dividing the total milligrams of the component collected in the organic resins by the water volume collected in the impinger train; the water volume data are corrected to standard gas volume. For example, during test 4 on the penta evaporator, 24,000 mg (24g) of penta was collected. The condensed water volume collected was 598 ml. This translates to .807 m^3 of water vapor at 23^{0}C and 1 atm, as follows:

$$598\text{g } H_2O \times \frac{1 \text{ mole}}{18.0\text{g}} \times \frac{22.414 \text{ liters}}{\text{mole } (0^0\text{C, } 1 \text{ atm})} \times \frac{296^0\text{K}}{273^0\text{K}} \times \frac{10^{-3}\text{m}^3}{\text{liter}}$$

Thus, the average concentration of penta leaving the evaporator during the test was:

$$\frac{24 \times 10^3 \text{ mg}}{0.807 \text{ sm}^3} \sim 3 \times 10^4 \text{ mg/sm}^3$$

System flowrates are based on plant operating information and field measurements. Between November 19 and December 31, 1980, the test plant generated 95,000 l (25,000 gal) of wastewater from the creosote process and 60,500 l (16,000 gal) from the penta process. The plant was on a 3-day/week treatment schedule for 18 days. The generation rates are calculated at approximately 5,200 l/day (1,400 gal/day) for the creosote process and 3,400 l/day (890 gal/day) for the penta process.

Between September 10 and November 18, 1980, 160,000 l (41,000 gal) of water were evaporated in the penta pan evaporator, and 20 barrels (approximately 550 lb, 250 kg, each) of sludge were recovered for disposal. Thus, approximately 32grams of sludge per liter of wastewater (0.27 lb/gal) were generated. For the creosote pan evaporator, the corresponding numbers are 280,000 l (73,000 gal) 24 barrels, and 22 g/l (0.15 lb/gal). From this, the rate of sludge generation is calculated to be 114 and 109 kg/day for the creosote and penta pan evaporators, respectively.

The driving force for vent emissions from the evaporator is boiling water vapor. Volume emission rates based on pure water vapor are calculated from the rate of volume change in the evaporators.

Given the diameter of the creosote evaporator (11 ft) and the average rate of change in the liquid height (0.997 inch/hr), the volume of water evaporated is calculated to be 5,370 l/day (1,420 gal/day), in agreement with the input rate of 5,200 l/day. The corresponding numbers for the penta evaporator are 3.66m (12-ft) diameter, 1.77 cm/hr (0.698 inch/hr), and 4,470

TABLE 9. PENTA PAN EVAPORATOR -- AVERAGE VALUES

Stream	Working solution	Oil/water recycle	Waste- water	Pan water	Pan sludge	Pan vent
Volume*			3,400 l/day	8x10^4 l	109 kg/day	6x10^3 sm^3/day
Concentration**	µg/ml	µg/ml	µg/ml	µg/ml	µg/g	mg/sm^3
Penta	44,000	42,000	7,000	80	62	10^4
Phenol	<200	<10	<10	0.6	1.2	200
Fluoranthene	430	3,300	1,500	4.3	2.0	600
Naphthalene	3,800	2,800	850	0.2	1.1	2x10^3
Benzo(a)anthracene	<100	480	250	1.9	0.5	70
Benzo(a)pyrene	<100	100	60	<0.1	0.05	<5
Benzofluoranthenes	<100	350	150	<0.1	0.2	10
Chrysene	<100	460	300	1.7	0.4	60
Acenaphthylene	170	260	950	0.2	0.05	100
Anthracene	230	750	290	0.6	0.5	300
Benzo(g,h,i)perylene	<200	18	<10	<0.1	0.1	<5
Fluorene	1,100	2,600	1,500	1.5	1.0	600
Phenanthrene	1,700	4,500	2,700	4.0	3.5	500
Dibenzo(a,h)anthracene	<200	4	<10	<0.1	0.1	<5
Indeno(1,2,3-c,d)pyrene	<200	22	<10	<0.1	0.1	<5
Pyrene	350	2,700	1,000	3.2	1.4	500
Benzene	<1	6	<10	<0.2	<0.2	<5
Toluene	18	54	<10	<0.2	0.3	<5
Ethylbenzene	23	10	<10	<0.2	<0.2	<5

*Solid and liquid flowrates are averages based on monthly production figures (kg/day or l/day). Gas volumes are based on average daily decreases in tank volume (sm^3/day).

**Concentration units are ppm w/w for solids and liquids, and at 23^{o}C, 1 atm for gases

TABLE 10. CREOSOTE PAN EVAPORATOR -- AVERAGE VALUES

Stream	Working solution	Oil/water recycle	Waste-water	Pan water	Pan sludge	Pan vent
Volume*	--	--	5200 l/day	40000 l	114 kg/day	7300 sm^3/day
Concentration**	μg/ml	μg/ml	μg/ml	μg/ml	μg/g	mg/sm^3
Penta	17,000	2,500	10	6.2	260	2
Phenol	400	1,100	6	23	30	30
Fluoranthene	32,000	23,000	80	25	590	23
Naphthalene	24,000	36,000	120	12	680	2500
Benzo(a)anthracene	20,000	16,000	35	16	390	1
Benzo(a)pyrene	600	1,800	4	6.7	91	<0.2
Benzofluoranthenes	650	520	10	3	190	0.6
Chrysene	15,000	12,000	30	10	240	0.8
Acenaphthylene	5,700	4,600	4	1.4	840	30
Anthracene	12,000	39,000	30	10	260	50
Benzo(g,h,i)perylene	<500	600	<5	<0.1	10	<0.05
Fluorene	36,000	37,000	63	27	660	400
Phenanthrene	37,000	32,000	110	34	1100	190
Dibenzo(a,h)anthracene	<500	1,000	<5	0.2	<10	<0.05
Indeno(1,2,3-c,d)pyrene	<500	900	<5	<0.2	16	<0.05
Pyrene	27,000	18,000	55	19	440	15
Benzene	26	<40	<0.1	<0.1	6.7	
Toluene	2.7	<25	<0.1	<0.1	1.4	
Ethylbenzene	<0.5	<25	<0.1	<0.1	0.3	

*Solid and liquid flowrates are averages based on monthly production figures (kg/day or l/day). Gas volumes are based on average daily decreases in tank volume (sm^3/day).

**Concentration units are ppm w/w for solids and liquids, and at 23°C, 1 atm for gases l/day (1,180 gal/day) reasonably in agreement with the 3,400 l/day input. The liquid volumes are converted into the following gas volumes:

- 7.3×10^3 sm^3/day from the creosote evaporator
- 6×10^3 sm^3/day from the penta evaporator

A summary of sampling times and volumes is given in Table 11.

5.1.4 Material Flow in Evaporators

Material flow calculations made at each evaporator are shown in Tables 12 and 13. Volume flowrates are the average daily rates calculated in the previous section. Values for the gross stream mass are in kg/hr, including water from the vents; values for individual components are in g/hr.

Data is presented in two formats: for the first the air emissions rate is given for each separate test, Tables 3 to 8. Secondly the component maximum and minimum are presented. The high vent rate uses the highest concentration of the component observed during testing, while the low value is from the lowest concentration observed. In all cases the average volume rate of water boiled off is used.

Since the amount of time during the evaporation cycle that each component is emitted at a measured concentration is not known, a time-weighted average is not available. The emitted material cannot be estimated as the difference between input and sludge output due to a quantity of recycled preservative oil removed. For the actual test run periods a summary of emitted organics is given in table 14. The hourly rates indicate that large quantities of organics are emitted for short periods of time. In addition, for the creosote evaporator, emissions were measured at 10:05 to 10:50 a.m. and 1:02 to 1:35 p.m. on September 25th. The two rates, 1,100 and 960 g/hr, indicate that over half of the daily organic charge for that specific day (947 mg/ml at 5,200 l/d = 4,924g) was emitted in the period measured -- 1,100 + 960/2 at (3.13 hr) = 3,224g.

The significant finding from the data is that a larger quantity of materials is charged to evaporators than was reported by EDG(1) as typical wastewater. (See Table 15 for comparisons.) In plant A's case this occurs because the evaporator is used as an in-plant dewatering device where the oily preserving material is returned to the process.

5.2 MODELS FOR THERMAL EVAPORATION

Negligible organic emissions would be predicted to be emitted to the atmosphere from thermal (pan) evaporation based on ideal solution vapor pressures (Raoult's law), and classical diffusion and mass transport theory. Result of previous laboratory(2) work indicated that such predictions might be wrong. In that report a higher level of emissions were suggested by postulating a hypothetical model applying regular solution theory and activity coefficients. This model would predict an increase in the emission rates by

TABLE 11. SAMPLING DATA

Location/ run number		Date	Start time	Stop time	Sample time	Water volume* (ml)	Water volume** (sm^3)
Penta	2	9/24/80	1208	1238	30	1302	1.758
	3	9/25/80	0806	0825.5	19.5	973	1.314
	4	9/26/80	1135	1150	15	598	0.806
Creosote	2	9/24/80	1451	1547	56	1130	1.524
	3	9/25/80	1005	1050	45	762	1.028
	4	9/25/80	1302	1313.5	11.5	946	1.275

*Liquid

**Gas at 23°C and 1 atm (73°F and 760 mm Hg)

TABLE 12. CREOSOTE PAN EVAPORATOR -- MATERIAL FLOW

Stream name Component	Wastewater in (g/hr)	Sludge out (g/hr)	Obs high pan vent out (g/hr)	Obs low pan vent out (g/hr)	Other Obs pan vent out (g/hr)*
Stream (x 10^{-3})	217	4.8	--	--	223 ave.
Penta	2.2	1.2	0.81	0.045	0.68
Phenol	6.5	0.14	17	0.015	14.5
Fluoranthene	17	0.01	7.5	6.0	5
Naphthalene	26	3.3	810	60	675
Benzo(a)anthracene	7.60	1.9	0.35	0.12	0.35
Benzo(a)pyrene	0.87	0.44	0.09	0.015	0.05
Benzofluoranthenes	2.2	0.91	0.39	0.05	0.18
Chrysene	6.5	1.2	0.36	0.090	0.3
Acenaphthylene	0.87	4.03	13	2.2	7.2
Anthracene	6.5	1.3	17	9.6	17
Benzo(g,h,i)perylene	1.1	0.05	0.015	0.015	--
Fluorene	13	3.2	150	33	137
Phenanthrene	24	5.3	65	29.5	50
Dibenzo(a,h)anthracene	1.1	0.002	<0.015	<0.015	--
Indeno(1,2,3-e,d)pyrene	1.1	0.002	<0.015	<0.015	--
Pyrene	12	2.1	4.8	3.9	3.2
Benzene	<0.022	0.032	--	--	--
Toluene	<0.022	0.0067	--	--	--
Ethyl benzene	<0.022	0.0014	--	--	--

* Three values were obtained by separate measurement -- high, low and the third or "other" value.

TABLE 13. PENTA PAN EVAPORATOR — MATERIAL FLOW

Stream name Component	Wastewater in (g/hr)	Sludge out (g/hr)	Obs high pan vent out (g/hr)	Obs low pan vent out (g/hr)	Other Obs pan vent out (g/hr)
Stream mass (x 10^{-3})	142	4.5	--	--	186 ave
Penta	990	0.3	7500	0.42	0.85
Phenol	1.4	0.0005	160	ND	0.16
Fluoranthene	210	0.01	420	0.25	1.3
Naphthalene	120	0.005	1500	0.50	0.75
Benzo(a)anthracene	36	0.0023	50	0.07	0.07
Benzo(a)pyrene	8.5	0.0002	ND	ND	--
Benzofluoranthenes	21	0.0009	10	ND	--
Chrysene	43	0.0023	50	0.07	0.65
Acenaphthylene	135	0.0002	340	ND	0.32
Anthracene	41	0.0023	190	0.04	0.58
Benzo(g,h,i)perylene	<1.4	0.0005	ND	ND	--
Fluorene	210	0.0045	430	ND	0.78
Phenanthrene	380	0.0016	380	0.25	2.3
Dibenzo(a,h)anthracene	<1.4	0.00045	ND	ND	--
Indeno(1,2,3-c,d)pyrene	<1.4	0.00045	ND	ND	--
Pyrene	50	0.0063	350	0.2	0.8
Benzene	<1.4	0.0009	ND	ND	--
Toluene	<1.4	0.00004	ND	ND	--
Ethyl benzene	<1.4	0.0009	ND	ND	--

TABLE 14. EMITTED ORGANIC COMPOUNDS: PNAs, PENTA AND PHENOL COMBINED

	Creosote Evaporator (g/hr)	Penta Evaporator (g/hr)
Average daily rate fed to evaporators	130	2,300
Exhaust emissions rates measured		
Minimum	140	1.8
Maximum	1,100*	11,400*
Other sample	960*	8.0

*Measurements taken shortly after new charge addition

TABLE 15. COMPARISON OF AVERAGE PLANT WASTEWATER COMPOSITION AND PLANT A SPECIFIC LOADING

	(g/m^3 Wood treated)		
Wood Preserving Plant	PNAs	Penta	Phenol
Average values based on EGD data	2.22	1.22	.0076
Plant A			
Penta process	440	347	.50
Creosote process	56.8	0.98	2.90

several orders of magnitude which would then be sufficient for field measurement and verification. The field tests that were subsequently made and reported, verified that organic emissions do occur at a significant level.

Although study of the field data reveals a wide variation in the observed concentrations of organics in the emissions, these concentrations were well above the level that would be predicted using Raoult's law. Because the sampling times varied with respect to the evaporation cycle and the filling process was not continuous, a closer inspection of the process was made and an analysis of expected phenomenon produced a new model for predicting emissions.

5.2.1 Process Description and Modeling

Thermal evaporation is similar to laboratory batch steam distillation: wastewater is transferred to the evaporator, internal heating is applied by steam coils, and after a given period of time, more wastewater is put into the evaporator. As organics are driven out, their concentration in the system decreases. When the concentration of a specie falls to zero in most of the water, it falls to zero in the emission. Therefore, the concentration of the emitted specie is cyclic: the average concentration measured during a given test depends on where in the evaporation cycle the sample was taken.

Four physical regimes for evaporation have been identified:

- Static evaporation (ideal or regular solution)
- Steam distillation
- Controlled mass transfer evaporation from an infinite sink
- Flash evaporation

A qualitative description of the model follows with a brief mathematical description and sample calculations for each mechanism. Observed values are then compared to predicted values for each mechanism involving one compound.

Qualitative Description--

Thermal evaporation of organic components from a wastewater matrix can be modeled as a series of physical processes. Each mechanism depends on the phase distribution of the component under study. At the beginning of the cycle, the component is distributed among sludge, water, and oil. Steam distillation deminishes the component in the (partially miscible) oil phase. The infinite source mass transfer mechanism then operates until the component can no longer be stripped significantly from the sludge. Finally, the static evaporation mechanism operates until the component has been stripped from the water or a new cycle begins. A diagram of the process is shown in Figure 3. An expected gas phase concentration plot is shown in Figure 4.

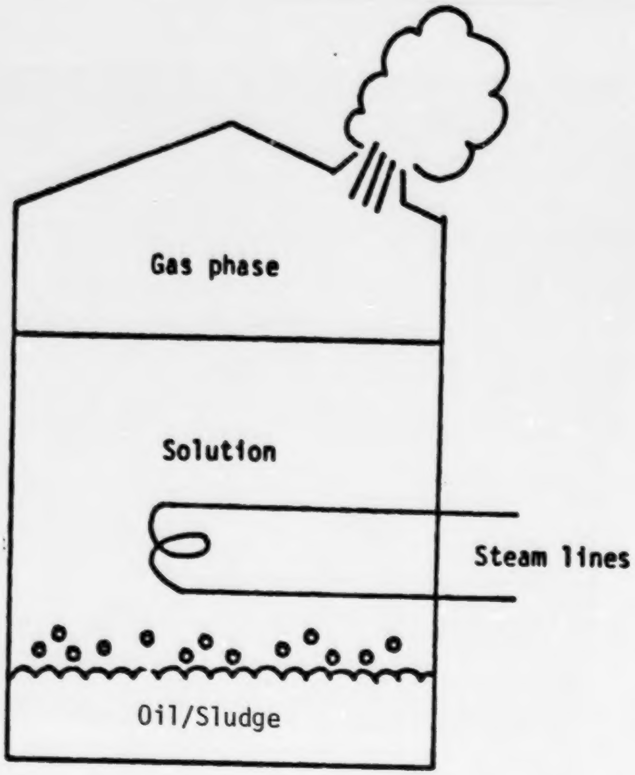

Gas phase
Solution
Steam lines
Oil/Sludge

Figure 3. Thermal evaporation system.

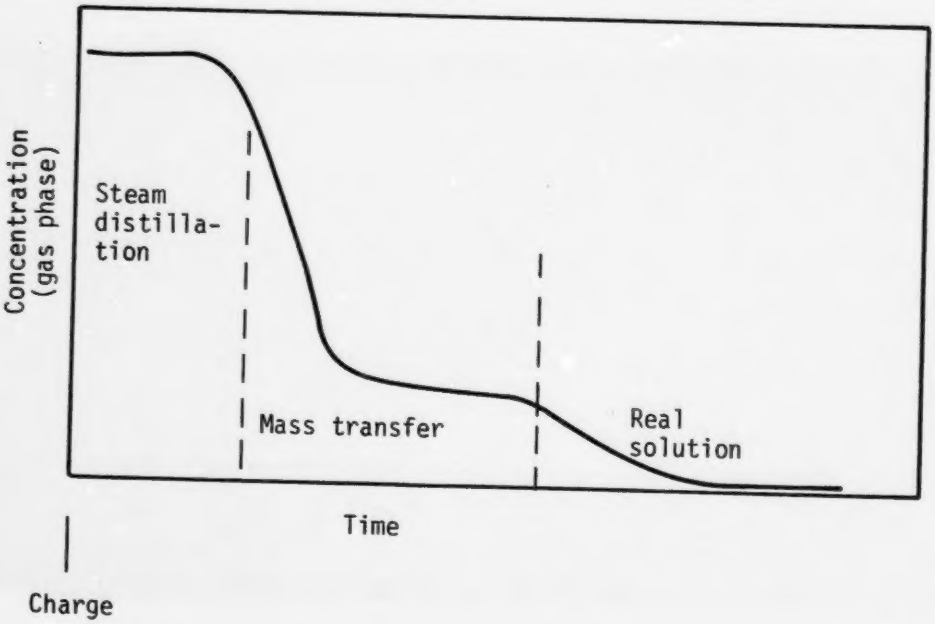


Figure 4. Thermal evaporation cycle.

A summary of the model follows:

- When water and component A exist as two partially immiscible liquids, steam distillation of component A occurs
- When the sludge can act as an infinite source of component A, the mass transfer rate from sludge to liquid to gas determines its concentration in the gas phase
- When component A is present solely in solution, static evaporation determines its approximate concentration in the gas phase
- Flash evaporation occurs only when the heat source is uncovered and well above the boiling point of the wastewater
- The duration of each mode differs for different components

Steam Distillation--

Immediately after charging, component A may exist as a partially miscible oil. If it does, its concentration in the gas phase is approximated by the pure steam distillation formula below:

$$\frac{W_A}{W_{H_2O}} = \frac{M_A\, P_A^o}{M_{H_2O}\, P_{H_2O}^o}$$

where W_A = weight of component A in vapor phase

W_{H_2O} = weight of water in vapor phase

M_A = molecular weight of component A

M_{H_2O} = molecular weight of water

P_A^o = partial pressure of pure A at boiling temperature of mixture

$P_{H_2O}^o$ = partial pressure of water at boiling temperature

Calculations for various components and tests in Tables 16 and 17 show a few compounds very near steam distillation concentrations and some very far away. The lower the solubility and the higher the concentration (in the incoming wastewater), the closer the component will be to the steam distillation concentration. The test time is also critical as shown by the differences between the penta pan evaporator tests 3 and 4. Test 3 was conducted just prior to the start of a new cycle, while test 4 was begun shortly after a new wastewater charge was placed in the evaporator.

TABLE 16. PENTA PAN EVAPORATION -- STEAM DISTILLATION MODEL

Component	Weight Ratio $\frac{W_A{}^*}{W_{B**}}$ PRED	Test 3 $\frac{W_A}{W_B}$ OBS	Test 3 $\frac{\text{OBS}}{\text{PRED}}$	Test 4 $\frac{W_A}{W_B}$ OBS	Test 4 $\frac{\text{OBS}}{\text{PRED}}$
Penta	0.038	4.6×10^{-5}	1×10^{-3}	0.04	1
Phenol	0.25	10^{-6}	4×10^{-6}	7×10^{-4}	3×10^{-4}
Naphthalene	0.18	4×10^{-6}	3×10^{-5}	8×10^{-3}	5×10^{-2}
Anthracene	0.013	3×10^{-6}	2×10^{-4}	10^{-3}	9×10^{-2}
Fluorene	1.5×10^{-3}	4×10^{-6}	3×10^{-3}	2×10^{-3}	1.2
Phenanthrene	5.2×10^{-3}	10^{-5}	2×10^{-3}	2×10^{-3}	0.4
Pyrene	1.4×10^{-4}	4×10^{-6}	3×10^{-2}	2×10^{-3}	1.3

*A is the component listed

**B is water in this case

TABLE 17. CREOSOTE PAN EVAPORATION -- STEAM DISTILLATION MODEL

Component	Weight Ratio	Test 2		Test 3	
	$\frac{W_A}{W_B}$ PRED	$\frac{W_A}{W_B}$ OBS	$\frac{\text{OBS}}{\text{PRED}}$	$\frac{W_A}{W_B}$ OBS	$\frac{\text{OBS}}{\text{PRED}}$
Penta	0.041	9×10^{-5}	2×10^{-3}	3.7×10^{-6}	9×10^{-5}
Phenol	0.24	2×10^{-5}	8×10^{-5}	7.9×10^{-5}	3.3×10^{-4}
Naphthalene	0.16	2.7×10^{-4}	1.7×10^{-3}	3.7×10^{-3}	0.023
Anthracene	0.013	4.3×10^{-5}	3×10^{-3}	9.2×10^{-5}	0.007
Fluorene	1.6×10^{-3}	1.5×10^{-4}	0.096	7.4×10^{-4}	0.46
Phenanthrene	2.3×10^{-3}	1.3×10^{-4}	0.056	2.6×10^{-4}	0.11
Pyrene	1.2×10^{-4}	2.1×10^{-5}	0.18	1.7×10^{-5}	0.16

Mass Transfer Limited Emissions--

The concentration of component A in the gas phase falls as the concentration in the solution falls: the emission rate also falls, assuming the water evaporation rate remains constant. Given sludge with a high concentration of component A (an infinite source), material dissolves from this source into solution at an increasing rate as the concentration in solution falls. At a certain concentration, the transfer rate from source to water become equal to the rate of transfer from water to air.

Over an interval of time, the average concentration of component A emitted (assuming evaporation volume change is negligible) is given by:

$$\frac{V_1(C_{AS} - C_A)}{V_g} = C_{Ag}$$

where V_1 = volume of wastewater in evaporator (liters)

C_{AS} = saturation concentration of A (mg/l)

C_A = steady state concentration of A (mg/l)

V_g = volume of water evaporated (liter)

C_{Ag} = concentration of component A in emission (mg/l)

From the analytical data, only the creosote pan evaporator sludge contains sufficient material to act as an infinite source.

Pure Static Liquid Evaporation--

Pure static liquid evaporation models are based on gas phase diffusion calculations assuming that the source concentration is constant and the driving force for transfer is pure vapor pressure. The classical approach for determining vapor pressure (and therefore gas phase concentration) is to use Raoult's law for ideal solution:

$$P_A = P_A^o X_A$$

where P_A = partial pressure of component A

P_A^o = partial pressure of pure component A at the temperature of the solution

X_A = mole fraction of component A in solution

This approach assumes that the solution is ideal, that solute and solvent do not interact, that the solute and solvent molecules are approximately the same size, and that the concentration of the solute is well below saturation. When such is not the case (as is obvious in the pan evaporation system), a regular solution theory is invoked; an activity coefficient of the solute-solvent system is incorporated into the formula:

$$p_A = p_A^o x_A \gamma_A$$

The activity coefficient, γ, is a measure of the departure from the ideal (Raoult's law). For $\gamma > 1$, there are positive deviations, and for $\gamma > 1$, negative deviations. Hydrocarbon/water systems almost universally have positive deviations. Predicted deviations for the system studied here are orders of magnitude greater than one.

Flash Evaporation--

When wastewater is flash-evaporated, the concentration of a given component in the gas phase equals its concentration in the liquid phase. The emission rate is equal to the evaporation rate of water times the component concentration in the water.

5.2.2 Comparison to Predictions

The predicted emission concentrations for each mechanism during the six tests is given in Table 18. These values are for naphthalene, a major component in both the creosote and the penta streams. The observed values are much higher than is predicted by classical evaporation theory, but lower than the predicted steam distillation values.

5.3 CONCLUDING EFFECT OF PAN EVAPORATION

A fundamental factor of plant emissions is the charging schedule of the evaporators by specific wastewaters. Such a schedule will determine the specific plant's environmental loading frequency and the cyclic nature of the emitted mass. This cyclic nature is the result of the once or twice-a-day charging of the evaporators from the oil/water separators. The emission rate of the organics in total and of specific components is on a charge frequency cycle.

The results of this study conclusively confirm that all types of organic species analyzed in the wastewater stream are emitted to the atmosphere upon pan evaporation. Furthermore, for the creosote load on 9/25 (the only charge that was tested twice for emissions) most of the mass of those organics were emitted. The quantity returned in recycled treating oil to the separators was not documented.

The total amount of organics emitted strongly depends on the effectiveness of the oil/water separator. The prior EPA inventory on wood preserving wastes estimated that slightly less than 100 metric tons of volatile organics materials were contained in wood preserving industry wastewaters that required treatment.(2) This quantity would be exceeded if the treating waste material contained in wastewater increased above the typical average values established for the industry. Such an event could occur at any plant that failed to maintain effective oil/water separation or

TABLE 18. COMPARISON OF PAN EVAPORATOR MODELS FOR NAPHTHALENE (g/sm^3)

Test number	Penta evaporator			Creosote evaporator		
Mode	2	3	4	2	3	4
Pure steam distillation	130	130	130	120	120	130
Limited mass transfer (sludge to water to gas)	9	14	16	3.2	3.4	3.1
Flash evaporation	3×10^{-4}	7×10^{-5}	2×10^{-4}	1×10^{-2}	7×10^{-3}	5×10^{-3}
Pure static liquid (ideal solution)	7.7×10^{-6}	1.9×10^{-6}	5.6×10^{-6}	2.2×10^{-4}	1.7×10^{-4}	1.1×10^{-4}
Pure static liquid (regular solution)	1.5	0.4	1.1	44	34	22
Observed	2×10^{-3}	3×10^{-3}	6.0	0.2	2.8	2.2

else purposefully discharged spent treating solution at a rate higher than typical. One example of such an increased impact occurred for plant A. The emission of organic material (phenols and PNAs) from this plant -- using two evaporators -- which varied widely from 0.15 to 12.3 kg/hr for the three test periods, indicates the industry can generate emissions of significant quantity.

Residue values given in Tables 12 and 13 indicate the solid waste still contain compounds which can adversely impact the environment. These values are for the residue that is disposed by containerized landfill but does not include any oil fraction recycled to the preservating system. Chlorinated dibenzofuran (CDF) and dioxins (CDD) were detected in the sludge of a lagoon which has stored the wastewater prior to use of the evaporators (see section 8 for discussion of CDF and CDD). Quantities reported were CDD = 2,830 ng/g and CDF = 365 ng/g. The penta waste residues left after thermal evaporation are lower in organic aromatic compounds than the wastewater sludge. The reverse cases was found for creosote waste as there the sludge contain higher concentrations but much lower quantities of compounds than the wastewater.

SECTION 6

CHARACTERIZATION OF MULTIMEDIA IMPACTS FROM SPRAY EVAPORATION OF WOOD PRESERVING WASTEWATERS

This field test program was conducted at a wood treating plant (plant B) utilizing spray pond evaporation to reduce its wastewater volume. The program was designed to determine the organic components of the emissions from the spray pond, from the resulting sludge layer, as well as from the wastewater input. Each stream was qualitatively and semiquantitatively analyzed for organic compounds, including volatile organics, chlorinated dibenzo-p-dioxins, chlorinated dibenzofurans, chlorinated phenolic compounds, and polynuclear aromatic hydrocarbons.

6.1 PROGRAM DESCRIPTION

This program focused on determining if organic emissions were discharged to the air during evaporation and if the transport mechanism could be established. Possible mechanisms were simple evaporation and aerosol drift. A cryogenic sampling system and a resin trapping method of sampling were compared.

A cryogenic sampling system developed by the University of Arkansas was used to collect samples of the spray pond emissions. The sampling system collected six simultaneous samples at a single location at different heights above the pond surface. This program was focused on determining if organic emissions were discharged to the air during evaporation and on attempts to determine if the transport mechanism could be established: possible mechanisms were simple evaporation or aerosol drift.

6.1.1 Test Site

The wood treating facility selected for field sampling employed two treating cylinders using a closed steaming process. Both cylinders could treat wood using penta formulations; one cylinder also could use creosote. Wood products treated at the plant consisted almost entirely of Southern yellow pine in the form of utility poles and lumber. Wood treated during the 3-day test period was 406.4m^3 (14,357 ft^3) — see Appendix B.

Wastewater and byproducts generated from the treating process were discharged into discrete oil/water separators. Each of the two primary separator held 38,000 l (10,000 gal). Primary separation was carried out as a batch process with an average retention time of 18 hours. The tanks were operated manually, and the recovered treating formulation was returned to the appropriate bulk storage tank. Creosote wastewater was discharged directly into the spray pond. Wastewater from the penta oil/water separator was further treated by a three-zone gravity separator using a skimming device to recover any remaining penta residue, after which the wastewater was discharged into the spray pond.

The spray pond consisted of an unlined pond with a pumping station and seven spray nozzles. The sprays were operated 24 hrs/day when nozzles were functioning or unless local wind conditions caused excessive drifting of the spray.

Figure 5 presents a diagram of the spray pond showing its dimensions and the placement of spray nozzles. Pond water is circulated to the spray nozzles by a pump situated in the northeast corner of the pond.

6.1.2 Field Test Program

The sampling program conducted included each of these test activities:

- Qualification of atmospheric characteristics at the spray pond
- Air emission sampling at the spray pond using:
  - Cryogenic U-tubes
  - Tenax traps
  - XAD-2 cartridges
- Liquid grab sampling of spray pond wastewater
- Solids sampling of spray pond sludge

Table 19 presents a summary of the field test matrix for the sampling period.

The air emission samples were collected using a sampling train developed by the University of Arkansas. A complete description of this unit is contained in Appendix B. The train was used to collect cryogenics (water and organics collected in a cold trap), nonvolatile organics in XAD-2 resin traps, and volatile organics in Tenax traps. Temperature and wind vector information also was collected. Details of all equipment used are presented in Appendix B.

6.1.3 Data Collected

The data for the pond evaporation study is given in Table 20. The pond sludge samples were collected 2m from the waterline edge over a fortnight while pond water recycle was taken from the spray pump discharge. Influent wastewater was sampled only by compositing two grab samples taken during the short period of discharging separator (creosote and penta)

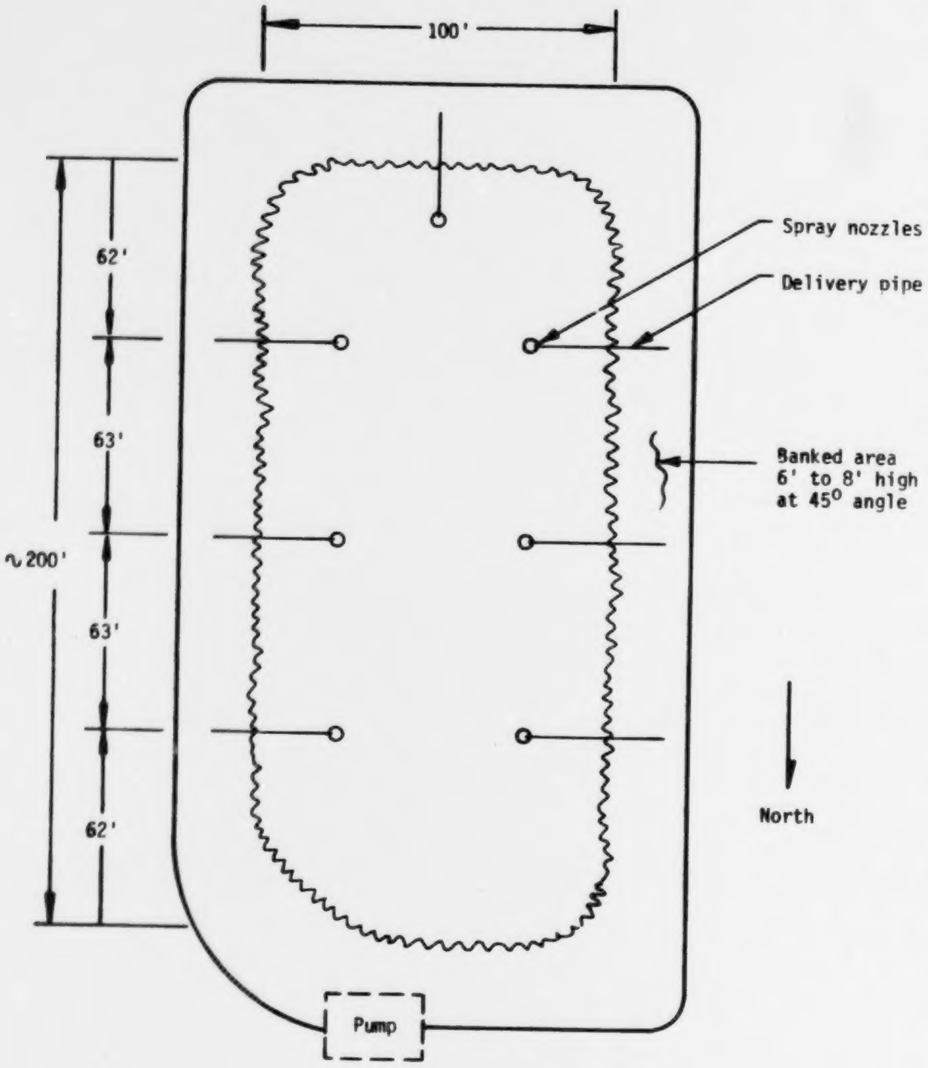

100'
62'
63'
63'
62'
~200'
Spray nozzles
Delivery pipe
Banked area
6' to 8' high
at 45° angle
North
Pump

Figure 5. Diagram of spray pond layout.

TABLE 19. SUMMARY OF SAMPLES COLLECTED

Sample	Air samples -- spray pond non-isokinetic sampling	Liquid samples -- composited grab sampling	Solid samples --* composited sludge sampling
1	4-XAD2, cryogenics and field volatiles using Tenax	1-composite	1-composite
2	4-XAD2, cryogenics and field volatiles using Tenax	1-composite	1-composite
3	4-XAD2, cryogenics and field volatiles using Tenax	1-composite	1-composite

*The three daily composite sludge samples were mixed for a single analysis.

TABLE 20. DATA FOR POND EVAPORATION

Component	Pond sludge+ (μg/g)	Wastewater input (μg/g)	Pond water recycle (μg/g)	Test 4* (total μg)
Pentachlorophenol	15,000	110	15	41, 5.2, 4.0
Phenol	<50	48	<0.1	
Fluoranthene	5,800	23	3	1.4, 1, 1
Naphthalene	1,500	120	3.1	ND, ND, ND
Benzo(a)anthracene	2,600	ND	2.5	ND
Chrysene	2,000	ND	3.4	ND
Anthracene	1,700	17	0.7	ND
Fluorene	5,600	58	1.8	ND, ND, ND
Phenanthrene	9,000	67	6.9	1.7, 1, 1
Pyrene	4,400	15	1.4	1.1, 1, 1
Other PNAs	490	<10	.3	
CDD	2.1	—***	—	
CDF	1.4	—	—	
Oil and grease	—	—	160	

*Test 4 sampled 6.1 l of air over 90 minutes before freeze-up. All other testing values were ND

**ND = Not detected (detection limit 1 μg)

***— = Not analyzed

+wet basis

wastewater into the pond. Results for the influent indicate undetected levels of several PNAs that were generally found in the pond recycle water and sludge. Those latter two sources represent water and sludge accumulated over a longer period of time and thus are more representative of usual conditions.

6.2 DISCUSSION OF RESULTS

Increases of component concentrations in the sludge and decreases in the recycled spray water as compared to the influent, strongly suggest the organic components concentrate. Without obtaining the quantity of sludge generated it is not possible to predict the quantity of organics that were emitted from the pond. Due to the slow buildup of sludge observed by mill personnel, it is apparent that the solids fraction cannot easily account for disposal of all the organics charged into the pond. Emissions other than those measured are expected. In addition, spray drift was observed by the sampling crew at the time of sampling thus. Since spray water contained organics but the air drift samples did not, the accuracy of the sample rate and detection limits were questioned.

Emission rates could not be determined due to the detection limits of the sampling and analytical methodology. While the University of Arkansas (UA) methodology is currently the best approach to determining organic emission rates from surface waters, the physical limits of spray pond evaporation and the sampling system prevent the detection of low and medium volatile compounds.

The best ambient air monitoring instrumentation available under optimum laboratory conditions can obtain levels of sensitivity to about 10 ppb (v/v) or methane equivalents of about 10 pg of total organics per analytical injection. Normal field monitoring instruments are good to about 1 ppm (v/v) for total organics. The QA procedure followed allows field samples to be analyzed at concentrations 10 times lower than the most sensitive methods or 1,000 times lower than the usual methods. For a compound such as phenol, this means a detection limit of about 1 to 5 ppb (v/v) in the gas phase of individual components.

The different molecular weights of the compounds under study make it easier to work with concentration units consisting of weight to sample volume. This gives the following sensitivities for the three sampling methodologies:

- Ambient monitoring — 10 ng/l of methane equivalent for total organics (no speciation)
- Field monitoring — 1 μg/l of methane equivalent for total organics (no speciation)
- UA methodology (FID) — 0.5 ng/l of individual components

Use of gas chromatography/mass spectrometry (GC/MS) with the UA sampling methodology decreases the sensitivity to about 50 ng/l. The sample volumes for the two standard methods are fixed by the instrumentation, while the sample volume of the UA system is limited by the moisture content of the gas stream: water vapor frozen out in the collection device eventually stops sample flow. This freeze up was anticipated to adversely affect the rotometer reading due to pressure changes, however the change was calculated to be only a minor inaccuracy.

In this study we drew 5 to 10 times the recommended amount of sample, increasing our sensitivity by approximately one order of magnitude.

Using Raoult's law of partial pressure a concentration of penta can be calculated in the range of 3×10^{-3} pg/l. Pure penta would be expected to exhibit concentrations of 3 ng/l (300 ng/sm^3). Although the normal sampling location for the UA system is at the water surface, this test required taking the samples on the berm, about 1m (3 ft) above water level. To offset the dilution occurring over this height, the samplers were run as long as possible (until the traps froze up). Thus the detection limits were only 2 to 3 times less than the maximum possible (see Table 21), but not nearly enough to make up for dilution. Dilution could be at least 10- to 20-fold over a distance of 0.6m 2 ft.

If further testing of very low level emissions from ponds are undertaken surface emissions may more effectively be sampled separately from spray drift sampling. Surface emissions can be analyzed from samples that collect all pollutants emitted into an enclosed surface air layer that excludes outside air. Such an enclosure has been developed using a plastic "bubble". Particle or aerosol drift can be better sampled by a high volume collection device which ensures higher sample volume than that collected at plant B. Drifting aerosol spray was observed at plant B and can be estimated from similar values well established for cooling towers. The pond evaporation rate is 6,800 l (1800 gal) per day. Using an evaporation/waterspray rate of 3 percent and drift factor of 0.1 percent of spray yields only 230 l/d of drifting spray. Since the total organic and phenol concentrations in the spray water are 34 and 5 μg/ml respectively, the organics and phenol emitted in drift would be 8 and 3-1/2 g/d respectively. Larger quantities are anticipated for days with high winds.

In conclusion, the methodology was insufficient to determine emissions off the ponds if there were any. Residue accumulations on the pond bottom contained PNAs, CDDs and CDFs. These toxic compounds were in significant amounts, however since no sediment layer sampling was initiated the quality of residue cannot be calculated.

TABLE 21. DETECTION LIMITS FOR PENTA — POND EVAPORATION

Test	Flow (ml/min)	Elapsed time (min)	Temperature (^oC)	Volume (sm^3)	Detection limit ppt (w/v) GC/MS (ng/sm^3)	Detection limit ppt (w/v) GC/FID (ng/sm^3)	Test type
1	66	23	8.5	1.6×10^{-3}	640	6.4	Cryogenic blank
2	66	135	6.4	9.4×10^{-3}	110	1.1	Tenax + XAD blank
3	66	180	8	13.0×10^{-3}	80	0.8	Tenax
4	66	90	12	6.1×10^{-3}	160	1.6	Cryogenic
5	66	42	12	2.9×10^{-3}	350	3.5	Cryogenic
6	66	69	8	4.8×10^{-3}	210	2.1	Cryogenic
7	66	94	3	6.6×10^{-3}	150	1.5	XAD
8	66	120	7	8.3×10^{-3}	120	1.2	XAD
9	66	120	14	8.1×10^{-3}	120	1.2	XAD
10	66	122	16	8.2×10^{-3}	120	1.2	Tenax
11	66	120	8	8.3×10^{-3}	120	1.2	Tenax

Maximum penta concentration = $\mu g/sm^3$ (30 ppb v/v)
Analytical sensitivity
Field GC/TVOC = 1 ppm
GC/MS concentrate = 1 μg/sample (1 ng injected)
GC/FID concentrate = 10 ng/sample (10 pg injected)

SECTION 7

CHARACTERIZATION OF DISCHARGES FROM THE DISPOSAL OF WOOD PRESERVING WASTES IN AN INDUSTRIAL BOILER

The EPA's rules promulgated in response to the Resource Conservation and Recovery Act (RCRA) encourages generators of hazardous wastes to control their wastes within plant boundaries. One disposal option is the thermal destruction of the waste in a steam boiler. This field test program was conducted at a wood preserving facility (plant C) using a 5 kg/sec (40,000lb/hr) pile-burning watertube boiler co-firing a mixture of wood waste and penta/creosote wastewater. The program was designed to determine the destruction and removal efficiencies of the organic compounds in the wastewater. Input materials (the wood waste and sludge) and output materials (mechanical hopper ash, baghouse ash, bottom ash and stack gases) were analyzed, and pertinent data for a material balance evaluation were collected. All samples were qualitatively and semiquantitatively analyzed for organic compounds, including chlorinated phenols, chlorinated dibenzo-p-dioxins, chlorinated dibenzofurans, and polynuclear aromatic hydrocarbons (PAHs).

7.1 PROGRAM DESCRIPTION AND RESULTS

Establishing material mass flow estimates was difficult since ash and fuel flowrates were not metered by the operator. However, estimates were made of each stream, and the destruction and removal efficiencies were calculated.

7.1.1 Test Site

The wood treating facility selected for field sampling employs six retorts using a steaming process to treat a variety of domestic and imported wood products. The process can treat wood with penta, creosote, or waterborne preservative formulations. Total wood treated during the test period, July 21 through 25, was 922m^3 (32558 ft^3).

Wastewater and byproducts generated from the individual treating processes are handled by discrete oil/water separators. The recovered preservative fractions are returned to bulk preservative storage tanks for reuse in the process. Separated sludges and wastewater are routed to a storage tank; when quantity is sufficient to ensure economic handling, the wastes go to the steam boiler for disposal. The boiler is fired by waste wood that is fed as sawn slabs or chips and sawdust. The waste sludge is pumped to the chip feeder and mixed with the dry wood chips or shavings in the screw feeder. Figure 6 presents a schematic of the plant wastewater/preservative recovery system. An estimated (23,000 to 36,000 l) 5,000 to 8,000 gal/day of wastewater is generated during normal treating operations.

The boiler, manufactured by Wellons Company, was designed to produce 5 kg/sec (40,000 lb/hr) of steam for space heat, the treating cycle steam, and other plant operations. The boiler unit, consisting of both a furnace and an additional cell, could be fired using both or fired separately, depending on plant process steam demand.

The boiler fuel supply system consisted of transfer and metering conveyors, wet and dry fuel silos, two metering bins for cell and furnace, and a constantly running screw conveyor to charge the fuel to the cell and furnace for burning. Both constant feed screw conveyors were modified to allow hog fuel to be mixed with sludge or wastewater from the treating plant. The furnace also was equipped with a ram charging device for loading irregular-shaped and oversized wood scrap into the boiler.

The unit is equipped with a multicone and two baghouses to reduce particulate emissions from the boiler. Figure 7 presents a schematic of the boiler plant including sampling locations. Figure 8 presents a photograph of the boiler plant. The plant personnel estimated that it burns 20 units/day of hog fuel during normal operation. (One unit = 200 ft^3 = 2,000 lbs dry Douglas-fir = 4,000 lbs Douglas-fir at 50 percent moisture = 16 MMBtu at 50 percent moisture.)

7.1.2 Field Test Program

The sampling program conducted included each of these tests:

- Determination of preliminary gas stream characteristics
- Isokinetic source sampling of boiler flue gas
- Total hydrocarbon determination of boiler flue gas
- Specific low-molecular-weight hydrocarbon determination of flue gas using gas chromatography (GC)
- Composite sampling of:
  - Boiler bottom ash
  - Multicone hopper ash
  - Sludge wastewater fuel

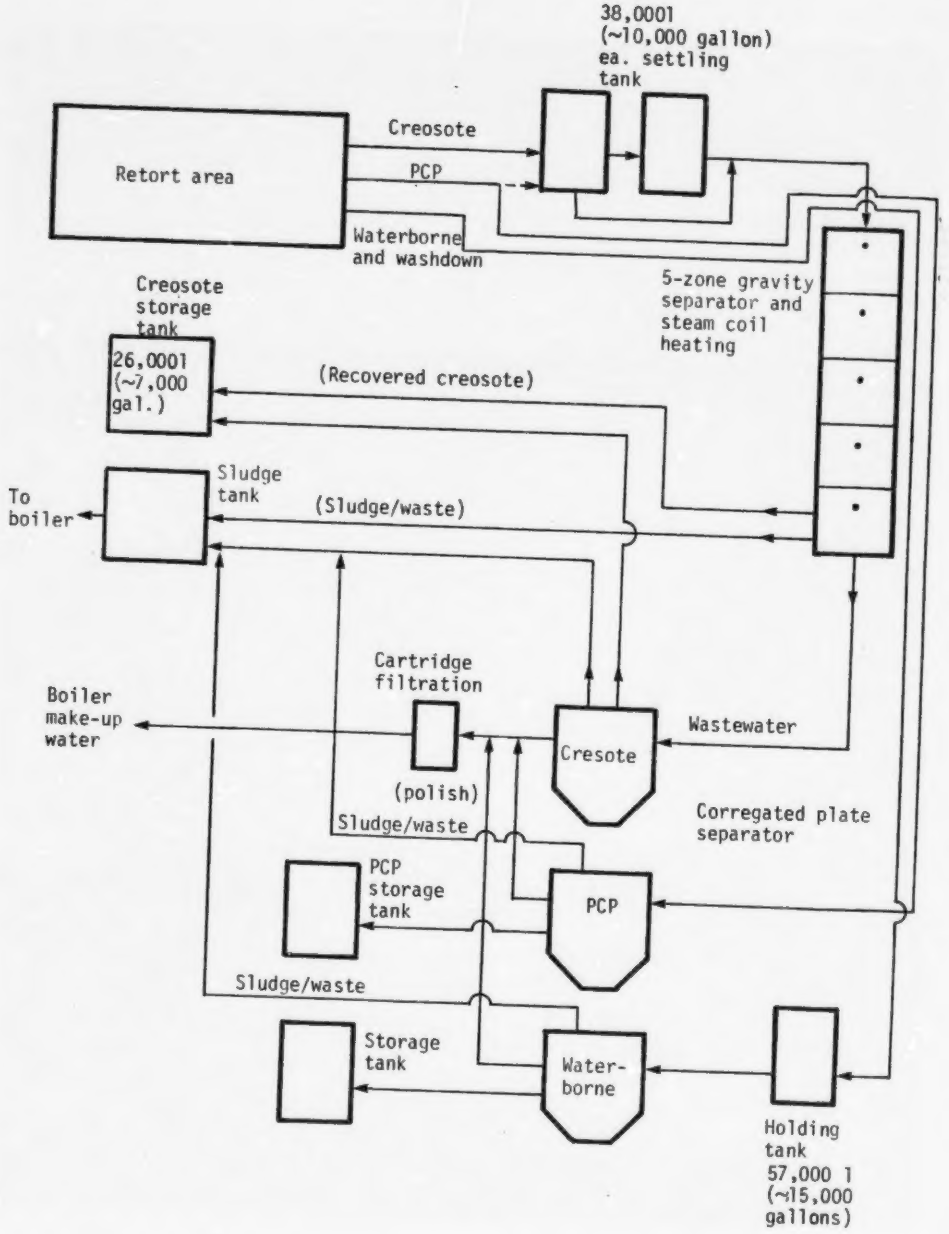

38,0001
(~10,000 gallon)
ea. settling
tank
Retort area
Creosote
PCP
Waterborne
and washdown
5-zone gravity
separator and
steam coil
heating
Creosote
storage
tank
26,0001
(~7,000
gal.)
(Recovered creosote)
To
boiler
Sludge
tank
(Sludge/waste)
Cartridge
filtration
Boiler
make-up
water
(polish)
Cresote
Wastewater
Corregated plate
separator
Sludge/waste
PCP
storage
tank
PCP
Sludge/waste
Storage
tank
Water-
borne
Holding
tank
57,000 1
(~15,000
gallons)

Figure 6. Schematic of plant wastewater/preservative recovery system.

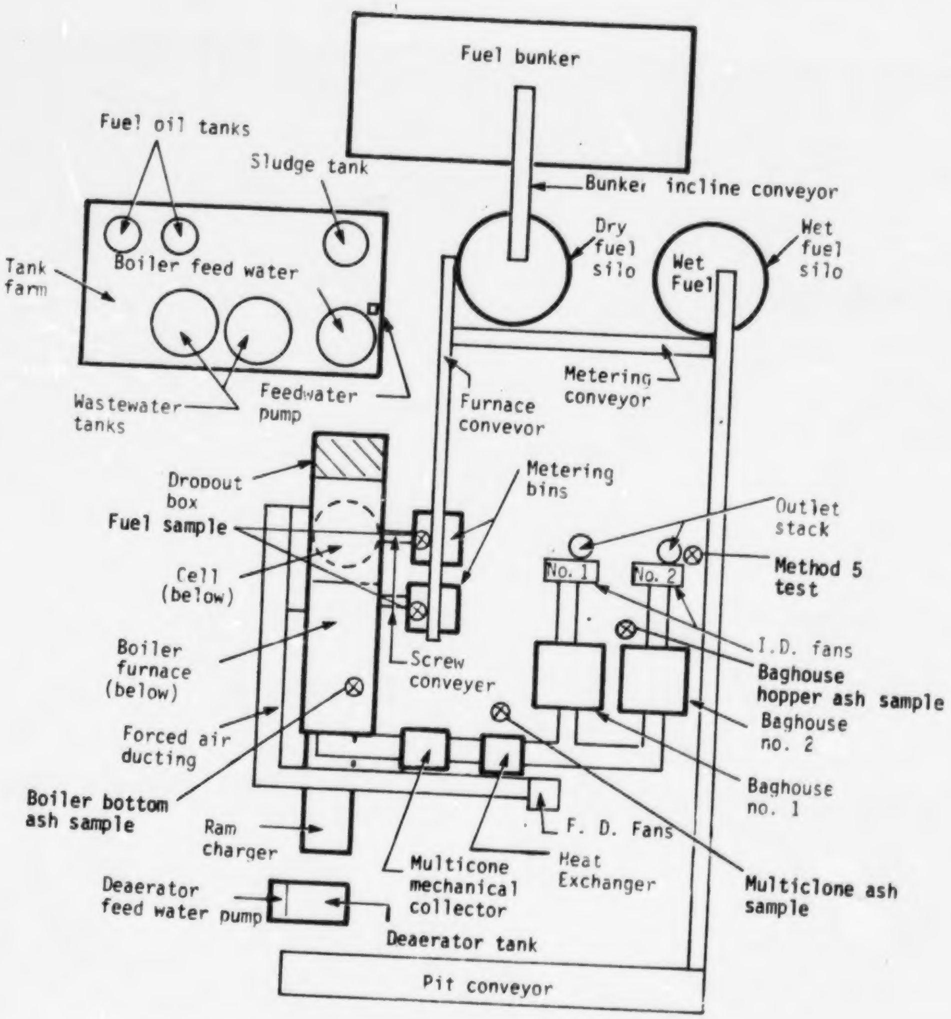

Fuel bunker
Fuel oil tanks
Sludge tank
Bunker incline conveyor
Dry fuel silo
Wet Fuel
Wet fuel silo
Tank farm
Boiler feed water
Metering conveyor
Wastewater tanks
Feedwater pump
Furnace conveyor
Metering bins
Dropout box
Fuel sample
Outlet stack
Cell (below)
No. 1
No. 2
Method 5 test
I.D. fans
Boiler furnace (below)
Screw conveyer
Baghouse hopper ash sample
Baghouse no. 2
Forced air ducting
Baghouse no. 1
Boiler bottom ash sample
Ram charger
F. D. Fans
Heat Exchanger
Multicone mechanical collector
Multiclone ash sample
Deaerator feed water pump
Deaerator tank
Pit conveyor

Figure 7. Schematic of boiler plant with sampling locations noted.

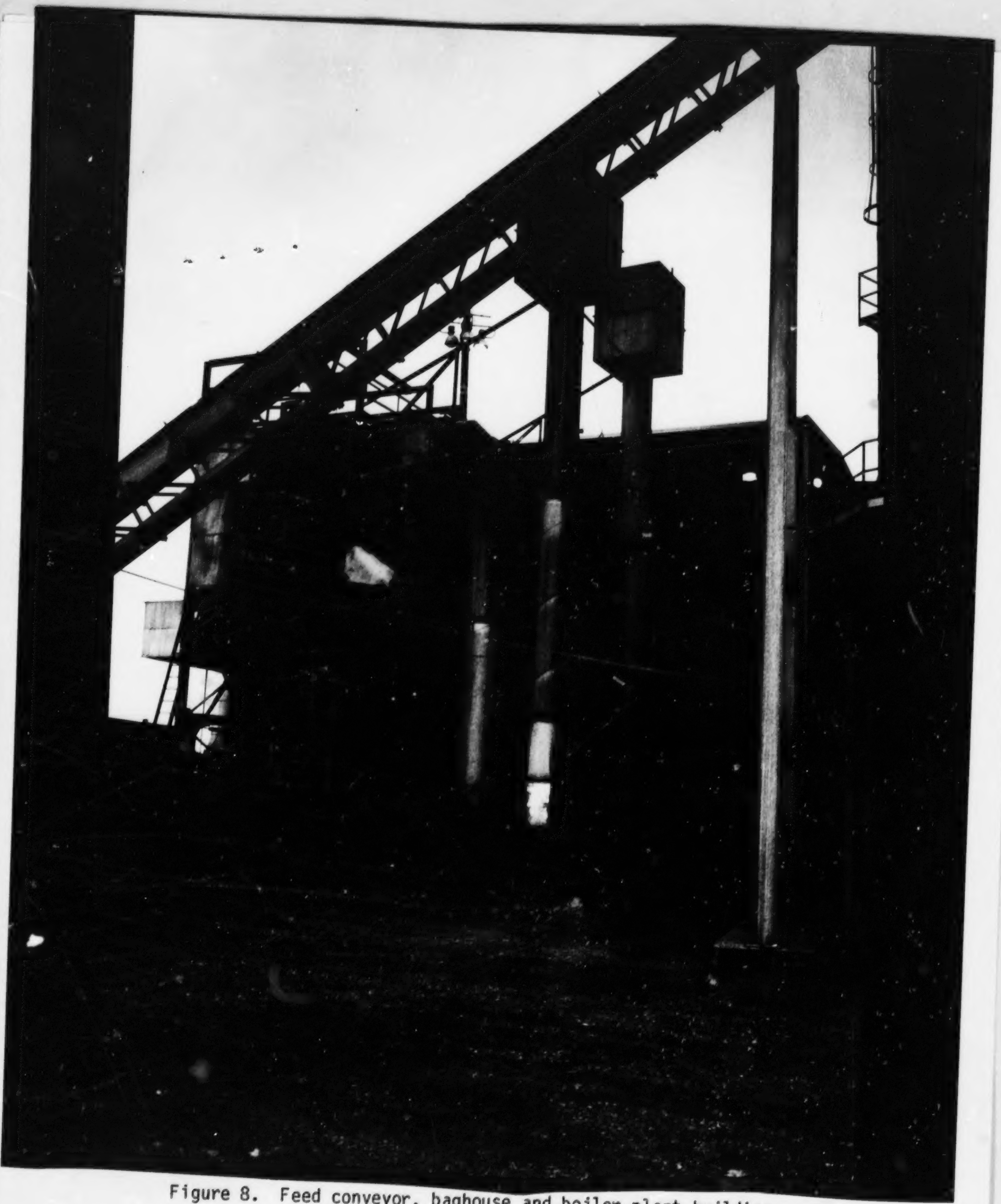


Figure 8. Feed conveyor, baghouse and boiler plant building.

- Grab sampling of:
  - -- Baghouse ash
  - -- Bulk penta in aromatic treating oil
  - -- Bulk creosote

The air samples were collected using an EPA Method 5 sampling train with XAD-2 resins for nonvolatile organic emissions. Volatile emissions were determined using field GC methods. The sample collection matrix included:

- Air samples
  - -- Outlet stack (1-XAD, GC)
- Solid samples
  - -- Wood waste and sludge (1-composite)
  - -- Boiler bottom ash (1-grab)
  - -- Mech. hopper ash (1-composite)
  - -- Baghouse (1-grab)

7.1.3 Data Presentation -- Organics and Inorganics

The concentrations of organic components in the various samples are shown in Table 22. The corresponding concentrations of trace elements are given in Table 23. Concentration units are in µg/g (ppm w/w) for the solids and liquid (sludge), and in units of µg/sm^3 (ppt w/v at 23°C and 1 atm). Components not detected are listed as less than (<) values if the number is a direct analytical measurement or as not detected (ND) if the value is calculated (i.e., averaged or requiring independent test data). NA means the component was not analyzed for.

The air emission rates for naphthalene and phenol are summarized in Table 24. Other components are not listed because they were not detected (detection limits are <10^{-5} g/sec). Stack sampling data are summarized in Appendix C.

7.2 MATERIAL DESTRUCTION EFFICIENCY

To determine the destruction efficiency of the hazardous waste components, a material balance for the compounds of interest was developed around the boiler facility.

The mass of ash components could not be easily measured due to physical constraints of the boiler system. However, the total ash quantity could be calculated. An initial effort was made to determine the ash quantity based on

TABLE 22. CONCENTRATIONS OF ORGANIC COMPONENTS IN INCINERATOR SAMPLES

Sample test	Feed sludge* (μg/g)				Bottom ash (μg/g)				Mechanical hopper (μg/g)				Baghouse dust (μg/g)				Stack gas (μg/sm^3)			
	2	3	4	Ave	2	3	4	Ave	2	3	4	Ave	2	3	4	Ave	2	3	4	Ave
Pentachlorophenol	470	260	80	270	0.5	0.5	0.5	0.5	0.05	0.5	7.4	2.7	1.0	1.0	1.0	1.0	ND**	ND	ND	ND
Phenol	1200	1000	1400	1200	0.1	0.8	0.6	0.8	0.1	0.1	0.1	0.1	0.5	0.2	0.3	0.3	4.1	2.7	2.3	3.0
Fluoranthene	2200	340	170	1350	92	15	1.4	36	0.5	0.6	1.7	0.9	0.7	0.2	6.2	2.4	ND	ND	ND	ND
Naphthalene	1300	1000	560	950	10	18	9.6	12.5	10.0	6.5	2.2	6.2	10	3.9	5.1	6.3	570	150	160	290
Benzo(a)anthrocene	160	120	27	100	7.6	0.6	0.1	2.8	<0.1	0.1	0.1	0.1	0.5	0.2	0.5	<0.4	ND	ND	ND	ND
Benzo(a)pyrene***	<20	30	<10	20	1.4	0.1	0.1	0.5	<0.1	0.1	0.1	0.1	0.5	0.2	0.5	<0.4	ND	ND	ND	ND
Benzo fluoranthene	52	64	14	43	9.3	0.9	0.1	3.4	<0.1	0.1	0.1	0.1	0.5	0.2	0.5	<0.4	ND	ND	ND	ND
Cryrene	180	120	28	110	1.2	0.7	0.1	0.7	<0.1	0.1	0.3	0.2	0.5	0.2	0.5	<0.4	ND	ND	ND	ND
Acenaphthylene	130	68	24	74	4.4	3.0	0.1	2.5	<0.1	0.1	0.1	0.1	0.5	0.2	0.5	<0.4	ND	ND	ND	ND
Anthracene	760	250	92	370	4.5	1.0	0.2	1.9	<0.1	0.1	0.2	0.1	0.5	0.2	0.5	0.4	ND	ND	ND	ND
Fluorene	1200	420	180	600	0.6	0.8	0.1	0.5	<0.1	0.1	0.1	0.1	0.5	0.2	0.5	0.4	ND	ND	ND	ND
Phenanthrene	1800	590	330	810	24	31	3.0	19	0.6	0.5	0.4	0.5	6.9	3.0	7.3	5.7	ND	ND	ND	ND
Pyrene	1200	310	140	550	29	7.9	0.4	12	<0.1	0.1	0.4	0.2	0.5	0.2	0.5	0.4	ND	ND	ND	ND
Benzenes	1	<1	<1	1	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND	ND	ND	ND
Toluene	12	3.7	9	8	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND	ND	ND	ND
Ethylbenzene	17	5.7	10	11	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND	ND	ND	ND

* Wet weight

** Calculated values below detection are ND

*** Analytical measurements not at detection are noted at (<)

TABLE 23. INORGANIC TRACE ELEMENT COMPOSITIONS IN INCINERATOR SAMPLES

Sample	Test	As	Be	Cd	Zn	Cr	Cu	Pb	Ni	Ag	Sb	Hg	Se	Tl
Feed sludge	2	6.8	0.001	<0.02	10.0	2.7	36	<1	<0.2	<0.06	<0.05	0.01	<0.05	<0.001
	3	3.5	$<9 \times 10^{-4}$	<0.02	7.0	2.6	48	<1	<0.2	<0.06	0.25	0.01	0.05	<0.001
	4	8.1	$<9 \times 10^{-4}$	<0.02	3.0	2.0	19	<1	<0.2	<0.06	0.16	0.02	0.10	<0.001
	Ave	6.1	ND	ND	6.6	2.5	34	ND	ND	ND	0.13	0.013	0.05	ND
Bottom ash	2	0.35	1.0	<0.02	2.0	1.0	29	<1	0.6	<0.06	<5.0	1.0	<5.0	<0.11
	3	40.5	0.7	<0.02	5.0	0.6	57	<1	0.5	<0.06	<5.0	2.0	10.0	<0.1
	4	73	1.0	<0.02	8.0	1.1	29	<1	0.4	<0.06	<5.0	0.9	10.0	<0.1
	Ave	38	0.9	ND	5.0	0.9	38	ND	0.5	ND	ND	1.3	10.0	ND
Mechanical hopper ash	2	0.02	2.0	0.1	90	1.9	85	100	0.3	<0.06	<5.0	3.0	<5.0	<0.1
	3	6.5	0.9	<0.02	40	2.0	120	10	0.3	<0.06	<5.0	4.0	<5.0	<0.1
	4	0.88	0.9	<0.02	30	1.8	70	10	0.2	<0.06	<5.0	2.0	<5.0	<0.1
	Ave	0.5	1.3	0.03	53	1.9	92	40	0.3	ND	ND	3.0	ND	ND
Baghouse dust	2	0.53	0.4	0.3	750	2.9	230	1500	0.4	0.1	25	5	10	<0.1
	3	11.4	0.4	0.4	750	4.4	305	1500	0.4	0.1	38	12	10	<0.1
	4	49	0.2	0.3	500	3.4	225	1200	<0.2	0.1	28	11	10	<0.1
	Ave	20	0.3	0.3	700	3.5	253	1400	0.3	0.1	30	9	10	ND

Units — µg/g (ppm w/w)

TABLE 24. RATES OF DISCHARGE AND EFFICIENCY OF DESTRUCTION FOR NAPHTHALENE AND PHENOL

		Feed (g/sec)	Bottom ash (g/sec)	Mech. hop. (g/sec)	Baghouse (g/sec)	Gas (g/sec)	Total out (g/sec)	Efficiency (percent)
Test 2								
	Naphthalene	0.10	$<5 \times 10^{-5}$	$<1 \times 10^{-4}$	$<5 \times 10^{-5}$	3.9×10^{-3}	3.9×10^{-3}	96.1
	Phenol	0.10	$<5 \times 10^{-7}$	$<1 \times 10^{-6}$	$<2.5 \times 10^{-9}$	2.9×10^{-5}	2.9×10^{-5}	99.97
	Solid rate	79	<5	<10	<5	(6.85)*		
Test 3								
	Naphthalene	0.08	$<9 \times 10^{-5}$	$<1.7 \times 10^{-4}$	$<1.9 \times 10^{-5}$	1×10^{-3}	1×10^{-3}	98.7
	Phenol	0.08	$<4 \times 10^{-6}$	$<1 \times 10^{-6}$	$<1 \times 10^{-6}$	$<1.9 \times 10^{-5}$	$<2 \times 10^{-5}$	>99.99
	Solid rate	79	<5	<10	<5	(6.85)*		
Test 4								
	Naphthalene	0.05	$<4.8 \times 10^{-5}$	$<2.2 \times 10^{-5}$	$<2.5 \times 10^{-5}$	1.1×10^{-3}	1.1×10^{-3}	97.8
	Phenol	0.11	$<3 \times 10^{-6}$	$<1 \times 10^{-6}$	$<1.5 \times 10^{-6}$	1.6×10^{-5}	1.6×10^{-5}	99.99
	Solid rate	79	<5	<10	<5	(7.0)*		

Assumptions: Feed rate, all cases = 79 g/sec sludge; ash quantity is 5 g/sec total, but some unburned organics were observed in the mechanical hopper thus <10g is used.

*Sm^3/sec (23°C and 1 atm)

indestructable material as tracers. Upon observation of data in Table 23, it is apparent that the partition of various metals into each ash component (bottom, hopper, baghouse) is dependent on the species, not the ash collecting component. In addition the large amount of metal component contributed by either the wood or sludge added a compounding complication to tracer analysis.

Only two organic compounds were detected in the stack emissions. The mass balance and destruction efficiency for these compounds were developed as follows:

- Measured rates were available for the feed and stack gas emissions. The feed rate was 72 l/sec with a density of 1.1 g/ml or 79 (range 66 to 99) g/sec. The gas volume ranged from 6.85 to 6.99 sm^3/sec (23°C and 1 atm). The exhaust gas particulate material was below detectable levels ($<10^{-3}$ g/sm^3 or $<10^{-2}$ g/sec), so solids in the gas stream were negligible.

- Rates for the three ash streams were not directly measurable; alternately the effect on mass balances was determined for maximum values based on the total ash generated. Total ash was calculated from the feed wood and sludge added. Ash composes 0.30 percent of Douglas-fir wood and 0.55 percent of Douglas-fir bark. Wood without bark was fed during the boiler test sequence. Based on 1,550 g/sec of wet wood and 79 g/sec sludge, the ash was calculated to be 5 g/sec. The mechanical hopper was observed to contain some unburned char thus a higher total quantity was assumed conservatively at 10g. Since the phenol and naphthalene losses that could occur through these ash amounts were too small to affect the destruction efficiency, their calculation provided an informative maximum.

Using these calculated rates, the mass flowrates of naphthalene and phenol (the only observed organic emissions) were derived and are presented in Table 24. The destruction efficiency also is presented, as calculated from the equation:

$$E = \frac{R_f\ C_{f,j} - \sum R_i,\ C_{i,j}}{R_f\ C_{f,j}} \times 100$$

where

R_f = feed rate of sludge
C_{fj} = concentration of j^{th} component in the feed
R_i = rate of discharge of i^{th} stream
C_{ij} = concentration of j^{th} component in i^{th} stream

Percent destruction of the two organic components of the sludge range from 96+ to >99.99 percent. These rates are the lowest values for any of the 16 organic constituents analyzed for in the stack gas. In fact, with the exception of naphthalene, all components were destroyed to 99.99 percent completion. The high stack value of naphthalene appears an oddity considering other component similarity in feed concentration and time-temperature requirements for destruction. Naphthalene contamination in other sample containers (discarded) is documented in Appendix C.

Table 25 compares the content of the raw creosote, the working penta solution, the sludge wastewater, and the fuel (sludge and wood chips) for representative compounds. Although incineration fuel is similar in relative proportion to the starting preservative solutions, the variations in relative quantities of compounds in sludge and penta are indicative of too few samples to provide precise values. The major changes through the process are dilution, first with water and then with wood chips.

As shown in the data tables, the ash samples contained ppm quantities of polynuclear aromatics. Whether these arise from unburned fuel or by partial combustion is not known. The absence of phenols in the bottom ash is evidence in favor of the latter hypothesis. Only naphthalene and low levels of phenols were detected in the XAD-2 cartridge samples; naphthalene was consistently detected. For further information see chromatograms in Appendix C.

To summarize, the incineration process gives rise to very low or undetectable levels of airborne volatile pollutants. The bottom ash from this process does contain significant concentrations of uncombusted material.

Section 8 discusses analysis of plant C samples for chlorinated dioxins and furans.

TABLE 25. SELECTED COMPONENTS IN WOOD PRESERVATIVE SOLUTIONS AND INCINERATION FUEL

Compound	Concentration ng/g			
	Creosote	Penta	Sludge	Fuel
Phenol	8,000	4,000	1,200	12
Naphthalene	1,700	660	900	18
Penta	1,700	16,000	260	15
Phenanthrene	37,000	1,200	850	18
Toluene	1,400	NA	8	NA

SECTION 8

CHARACTERIZATION OF CHLORODIBENZOFURANS AND CHLORODIBENZODIOXINS DISCHARGED FROM A BOILER CO-FIRING WOOD PRESERVING WASTES

The existence of dioxins and furans in combustion ash and wood preserving waste is well documented(2,6). Thus, as an effort to quantify the amount of these compounds in emissions or residues from the co-firing of wood and preserving waste sludge, analyses of the wastes, exhaust gas and three ash components was accomplished. Results of these analyses with input from three different laboratories are presented in this section along with a brief discussion of procedures used.

8.1 FURAN AND DIOXIN ANALYSIS OF STACK GAS, WASTE, AND ASH

Samples utilized in the chlorodibenzofuran (CDF) and chlorodibenzodioxin (CDD) analysis were the samples identified in Section 7. Abbreviations for various chlorinated homologs are listed in Table 26 along with the possible number of isomers of each. The analytical results of CDF and CDD are presented in Tables 27 to 32.

No CDFs or CDDs were detected in the air emissions. The detection limits were <10 $\mu g/m^3$ (10 ppt w/v).

Both CDFs and CDDs were found in the treating penta solution, waste sludge and the ash. Although these materials were detected, the quantity measured was not consistent and depended on the analyzing laboratory's procedures.

Ash sludge and penta in oil samples were analyzed by multiple laboratories using split samples. Tables 27 to 29 report values for Lab A while Table 32 reports results for Labs A, B and C. To better understand the values presented, the sample preparation procedures are compared in Table 33. Also it should be stated that the recovery reported by the three labs is quite different, varying between less than 40 percent and over 130 percent. Spike and recovery data for Labs A and B are given in Appendix C. Recovery for Lab C was reported as 50 to 80 percent but not documented during analysis.

For each of the listed homologs of CCD and CDF, typically only a single isomer was available for calibration. The total number of isomers was deduced by comparing the GC/MS properties of the standard to those unknown compounds exhibiting similar properties. However, since not all isomers of a given group were available for calibrating retention times, a given mass

TABLE 26. SUMMARY OF ABBREVIATIONS FOR CHLORODIBENZOFURAN AND CHLORODIBENZODIOXINS

Abbreviations	Name	Possible isomers
MCDF	Monochlorodibenzofuran	4
DCDF	Dichlorodibenzofuran	16
TrCDF	Trichlorodibenzofuran	28
TCDF	Tetrachlorodibenzofuran	38
PCDF	Pentachlorodibenzofuran	28
HxCDF	Hexachlorodibenzofuran	16
HpCDF	Heptachlorodibenzofuran	4
OCDF	Octachlorodibenzofuran	1
MCDD	Monochlorodibenzodioxin	2
DCDD	Dichlorodibenzodioxin	10
TrCDD	Trichlorodibenzodioxin	14
TCDD	Tetrachlorodibenzodioxin	22
PCDD	Pentachlorodibenzodioxin	14
HxCDD	Hexachlorodibenzodioxin	10
HpCDD	Heptachlorodibenzodioxin	2
OCDD	Octachlorodibenzodioxin	1

TABLE 27. CHLORODIBENZOFURAN AND CHLORODIBENZODIOXIN ANALYTICAL RESULTS FOR TREATMENT OIL (4.5 PERCENT PENTA IN OIL) -- LABS A AND B

Monomer of CDD or CDF*	Total number of apparent isomers**	Total detected*** (ng/g)	Minimum detectable concentration (ng/g)
MCDF	4	2 (180)$^+$	0.4
DCDF	2	2 (1800)	0.8
TrCDF	4	10 (ND)	1.2
TCDF	5	18 (ND)	0.1
PCDF	5	140 (920)	1
HxCDF	5	1800 (2700)	1
HpCDF	2	114 (3100)	1
OCDF	1	710 (4660)	3
MCDD	2	1.5 (i)	0.4
DCDD	2	2 (i)	0.8
TrCDD	2	3.5 (i)	1.2
TCDD	NR	1.1 (i)	0.5
PCDD	6	33 (i)	0.3
HxCDD	4	570 (1,540)	1
HpCDD	2	260 (17,100)	1
OCDD	1	4000 (>17,000)	3

*See table 8-1 for summary of nomenclature

**See text

***Not corrected for recovery, these concentrations represent minimum values

+Analysis reported by Lab B for monomer groups only isomers and detection limit not given

iInterferences too large to quantify

TABLE 28. CHLORODIBENZOFURAN AND CHLORIDIBENZODIOXIN ANALYTICAL RESULTS FOR DAY 2 COMPOSITE SLUDGE LIQUID -- LAB A

CDD/CDF*	Total no. of apparent isomers**	Total detected*** (ng/g)	Minimum detectable concentration (ng/g)
MCDF	4	0.6	0.2
DCDF	0	0	0.3
TrCDF	0	0	0.7
TCDF	0	0	0.1
PCDF	1	0.3	0.2
HxCDF	2	0.8	0.5
MCDD	1	0.2	0.2
DCDD	0	0	0.3
TrCDD	0	0	0.7
TCDD	0	0	0.9
PCDD	3	0.6	0.3
HxCDD	4	2.5	0.5

*See Table 7-6 for summary of nomenclature

**See text

***Not corrected for recovery, these concentrations represent minimum values; all sludge is wet weight

TABLE 29. CHLORODIBENZOFURAN AND CHLORODIBENZODIOXIN ANALYTICAL RESULTS FOR DAY 4 COMPOSITE SLUDGE LIQUID -- LAB A

CDD/CDF*	Total no. of apparent isomers**	Total detected*** (ng/g)	Minimum detectable concentration (ng/g)
MCDF	3	0.7	0.2
DCDF	0	0	0.4
TrCDF	0	0	0.9
TCDF	0	0	0.05
PCDF	1	0.5	0.2
HxCDF	3	8	2
HpCDF	2	7	1
OCDF	1	2	1
MCDD	1	0.6	0.2
DCDD	1	0.4	0.4
TrCDD	0	0	0.9
TCDD	0	0	0.9
PCDD	0	0	1
HxCDD	3	10	1
HpCDD	2	70	1
OCDD	1	230	1

*See Table 7-6 for summary of nomenclature

**See text

***Results corrected for recovery

TABLE 30. CHLORODIBENZOFURAN AND CHLORODIBENZODIOXIN ANALYTICAL RESULTS FOR DAY 3 COMPOSITE ASH -- LAB A

CDD/CDF*	Total no. of apparent isomers**	Total detected*** (ng/g)	Minimum detectable concentration (ng/g)
MCDF	3	90	0.1
DCDF	8	7.5	0.3
TrCDF	6	20	0.6
TCDF	8	1.2	0.05
PCDF	5	0.7	0.1
HxCDF	2	1	0.3
HpCDF	2	1.6	0.6
OCDF	1	1.2	1
MCDD	1	2	0.1
DCDD	5	1	0.3
TrCDD	5	5	0.6
TCDD	NR	0.8	0.2
PCDD	5	2.6	0.1
HxCDD	1	8.7	0.3
HpCDD	2	42	1
OCDD	1	96	1

*See Table 7-6 for summary of nomenclature
**See text
***Results corrected for recovery

TABLE 31. CHLORODIBENZOFURAN AND CHLORODIBENZODIOXIN ANALYTICAL RESULTS FOR DAY 4 COMPOSITE ASH -- LAB A

CDD/CDF*	Total no. of apparent isomers**	Total detected*** (ng/g)	Minimum detectable concentration (ng/g)
MCDF	3	5	0.1
DCDF	10	8	0.3
TrCDF	11	17	0.6
TCDF	8	3	0.1
PCDF	5	3	0.3
HxCDF	4	1.8	0.4
HpCDF	0	0	2
OCDF	0	0	1
MCDD	2	0.7	0.1
DCDD	4	0.5	0.3
TrCDD	4	6	0.6
TCDD	6	3.3	0.2
PCDD	4	6	0.3
HxCDD	3	10	0.4
HpCDD	2	4	2
OCDD	1	1	0.8

*See Table 7-6 for summary of nomenclature
**See text
***Results corrected for recovery

TABLE 32. CHLORODIBENZOFURAN AND CHLORODIBENZODOXIN ANALYTICAL RESULTS FOR DAY 2 ASH -- LABS A, B AND C.

	Lab-A			Lab-B						Lab-C					
	Composite[4]			Bottom Ash #10			Baghouse Ash #18			Bottom Ash #10			Baghouse Ash #13		
	AI[1]	TD[2]	MDL[3]	AI	TD	MDL	AI	TD	MDL	AI[1]	TD[2]	MDL[3]	AI	TD	MDL
MCDF	3	75	0.1	NR	ND	24	NR	29	27	NR[5]	NR	NR	NR	NR	NR
DCDF	8	25	0.3	NR	ND	42	NR	60	48	NR	NR	NR	NR	NR	NR
TrCDF	8	15	0.6	NR	ND	45	NR	ND	52	NR	NR	NR	NR	NR	NR
TCDF	7	7	0.5	NR	ND	29	NR	ND	34	NR	<5	5	26	900	5
PCDF	5	8	1.0	NR	ND	68	NR	ND	77	NR	<5	5	16	1,500	5
H_xCDF	5	5	1.0	NR	ND	115	NR	ND	132	NR	<5	5	11	150	5
H_pCDF	2	6	1.0	NR	ND	25	NR	ND	29	NR	<5	5	3	60	5
OCDF	1	2	1.0	NR	ND	71	NR	ND	163	NR	<5	5	1	6	5
TOTAL CDF		143			<420			<575			<5			2,600	
MCDD	1	1	0.1	NR	ND	102	NR	ND	117	NR	NR	NR	NR	NR	NR
DCDD	4	5	0.3	NR	ND	44	NR	ND	51	NR	NR	NR	NR	NR	NR
TrCDD	5	2	0.2	NR	ND	52	NR	ND	60	NR	NR	NR	NR	NR	NR
TCDD	4	4	0.2	NR	ND	47	NR	ND	54	1	10	5	8	960	5
PCDD	5	32	1.0	NR	ND	93	NR	ND	112	4	20	5	4	1,400	5
H_xCDD	5	81	1.0	NR	ND	165	NR	ND	189	3	40	5	6	2,000	5
H_pCDD	2	117	1.0	NR	ND	95	NR	ND	109	2	100	5	2	640	5
OCDD	1	200	1.0	NR	ND	198	NR	ND	226	1	140	5	1	210	5
TOTAL CDD		438			<800			<920			310			5,200+	

[1] Total number of apparent isomers
[2] Total detected (ng/g)
[3] minimum detectable limit (ng/g)
[4] Composited by weight 2:5 (bottom:flyash)
[5] NR -- not reported

TABLE 33. SAMPLE CLEAN-UP PROCEDURES

	LAB-A	LAB-B	LAB-C
Prewash	None	None	1N HCl
Extraction	Benzene 16 hrs	Benzene 24 hrs	Toluene 36 hrs
Cleanup			
Exchange	Hexane	Petroleum ether	Hexane
Wash	Base, acid	Base, acid	N.R.
Column	1 Silica base, acid 2 Alumina 1:1 CH_2Cl_2/HEX	Alumina 1:1 CH_2Cl_2/HEX	Alumina 1:1 CH_2Cl_2/HEX

chromatographic peak does not necessarily correspond to a single isomer of a given class; such peaks may represent more than one isomer. Hence, the authors selected the terminology "apparent isomers."

8.2 DISCUSSION OF RESULTS

Since extraction and cleanup and quality assurance procedures were quite different in the three laboratories, no detailed comparison or discussion of results will be made. Several general points are raised briefly as follows:

- Based on the results given it is apparent the treating solution of pentachlorophenol in oil, wastewater sludge, and resulting ash contain chlorinated furans and dioxins. In terms of specific monomers TCDD's are evidently generated in the process while OCDD's are reduced. This determination is based on an assumed ash generation rate of 5 g/hr and sludge feed of 79 g/hr. Wood inputs were not analyzed for CDD or CDF, but are assumed minor compared to pentachlorophenol sludge waste.

- The highly toxic isomer 2,3,7,8-TCDD has not conclusively been demonstrated as present and apparently is not in ash samples. See Appendix C for reported mass fragmentography and synthetic isomer standard curves.

- The toxicities of CDDs and CDFs are quite isomer-specific (see table 34). Thus, data useful for risk analysis must contain isomer data that is clearly independent of contamination. Staff chemists for all the labs are quite confident of the reliability of their reported values especially in light of the use of standard isomers.

- Values determined are in the range reported for combustion ash and especially of wood preserving waste ash from other sources -- see table 35. The fractions of bottom ash/flyash have TCDD values similar to values reported for precipitator/down stack ash fractions in Germany -- both in level and increasing ratio with smaller size.

- Ratios of TCDD/CDD and OCDD/CDD of the feed sludge (0 and .74-.76 respectively) and penta in oil (0 and .82 respectively) are typical of other penta environmental samples but also differ from flyash ratio enough to indicate composition changes.

- Measurements of MCDD, DCDD, and TrCDD monomers are significant as this is only the second time combustion sources measurements have had positive values reported.

- Toluene extraction may yield a cleaner concentrate than benzene, strengthening the apparent reliability lab C values.

- Recovery of spikes is dependent on both spiking isomer and time of spike in the procedure. These were not similar for the three labs.

Other information on CDD/CDF analysis and procedures is provided in the Appendix C.

TABLE 34. ACUTE TOXICITIES OF DIOXINS (7)

	LD_{50} (μg/kg)		
Substitutions with chlorine	Guinea pigs	Mice	Rats
None		$<50 \times 10^3$	$>1 \times 10^6$
2,8	>300,000		
2,3,7	28,440	>3,000	$>1 \times 10^6$
2,3,7,8	0.6-2.0	283.7	40
1,2,3,7,8	3.1	337.5	
1,2,4,7,8	1,125.0	>5,000	
1,2,3,4,7,8	72.5	825	
1,2,3,6,7,8	70-100	1,250	
1,2,3,7,8,9	60-100	>1,440	
1,2,3,4,6,7,8	7,180		
1,2,3,4,6,7,8,9		$>4 \times 10^6$	
Hexa (mixture)			$\sim 1 \times 10^5$
Octa (mixture)			$\sim 2 \times 10^6$

Interperitoneal

TABLE 35. COMPARISON OF CDD VAUES IN ASH REPORTED FROM COMBUSTION SOURCES(6)

Reporting source	TCDD	PCDD	H_xCDD	H_pCDD	OCDD	$\frac{TCDD}{CDD}$	$\frac{OCDD}{CDD}$
This project (Plant A)				(μg/g)			
Lab A (d-2)	4	32	81	117	198	.009	.45
Lab A (d-3)	.8	2.6	8.7	42	96	.005	.61
Lab A (d-4)	3.3	6	10	4	1	.10	.032
Lab C (d-2)							
Bottom ash	10	20	40	100	140	.032	.45
Baghouse (fly)	960	1,400	2,000	640	210	.18	.04
Multiple sources wood preserving waste ash			9–27	90–135	575–2,510	0	.8–.9
Lab combustion of penta (smoke)	5.2	14	56	172	710	.005	.74
Lab combustion of penta, 2,4,6 tri-, and 2,3,4,6-tetra-chlorophenol (ash)	17	58	74	18	6	.1	.035
Dow Chemical							
Oil/coal combination	38		2	4	24	.56	.35
Tar burner			8	92	300	0	.75
Tar, gas kiln			3	32	230	0	.87
Oil combustion (Swiss)	100	160	180	130	40	.16	.066
Municipal Incinerator (ng/m^3)							
New York (ng/m^3)	40-120						
Swiss	2	8	30	60	120	.009	.55
Canada	9	15	13	3	.4	.22	.010
Japan						.078	.31
						.19	.29
Germany							
Precipitator ash	25						
Downstack ash (ng/m^3)	300,000 (15,000)						

SECTION 9

EVALUATION OF FUGITIVE EMISSION AND RESIDUE SOURCES

For the purposes of this program, fugitive materials are defined as residues from:

- Solids settled in unlined lagoons
- Spillage and drippage from treating cylinders

or emissions from:

- Vapors released from the treating cylinder during unloading and charging operations
- Vacuum vent exhaust during the treating cycle
- Emissions derived when removing the accumulation of treating solution from valves, fittings, or open processing vessels

These sources of materials are of concern because of the opportunities for employees to contact the toxic compounds before dilution and because of their impact on ambient air quality or future land use.

When the treating cylinder (retort) is opened, any treating solution left in the vessel may spill onto the ground. If the retort is surrounded by a spill berm, the treating solutions are recovered and recycled to the system. However, if the treating solution is allowed to fall onto the ground, housecleaning activities could result in an accumulation of hazardous waste material. Similar minor waste accumulations occur from the solids fallout in unlined lagoons or holding ponds. The slow buildup of residue in large wastewater treatment lagoons can accumulate and remain hazardous after the lagoon is abandon -- see Section 5.3.

Low-molecular-weight organic compounds vaporize in the retort during the high-temperature preservative application. During charge changes, these organics are released as fugitive emissions through the open door of the retort, forming a dense white plume. The wood removed from the retort also emits material as a white plume that may exceed 40 percent opacity after 20 minutes. Qualitative and semi-quantitative organic analyses for specific pollutants in these emissions were expected to show the presence of benzene, toluene, phenol, and similar volatile and low-molecular-weight compounds.

Emissions from the vacuum exhaust and other retort vents also are of concern. Source tests at one mill measured 2.2 g/m^3 (0.95 grain/scf) of aerosol in 12.5 m^3/min (440 scfm) of gas from a vacuum pump vent. Steam conditioning released 44 g/m^3 of aerosol in a 13 m^3/min stream.

Finally, while fugitive emissions from preservative handling, transport, leaks, and valves can occur, no qualitative or quantitative data is available to characterize such emissions.

This section presents the component speciation results from fugitive emissions tests conducted at plant A and residues from plant B. Emissions from preservative handling, transport, leaks, and valves were not tested. Also the subjects of chemical losses from treated material or runoff from contaminated surfaces was not covered.

9.1 TREATING CYLINDER SPILLAGE AND DRIPPAGE

The treating facility tested employed two treating cylinders, and used penta and creosote preservatives. Samples of accumulated spillage and drippage were collected at the bottom of the penta and creosote treating cylinder access doors. Waste liquid was intercepted after falling from the cylinders but prior to ponding on the ground beneath. Two samples were obtained at each location at the beginning and after the field test period. Table 36 presents the qualitative organic analysis for these samples.

9.2 FUGITIVE EMISSION DURING UNLOADING AND CHARGING OPERATIONS

Air samples were collected during unloading and charging operations directly above the penta and creosote treating cylinder access doors. Sampling was performed using the modified EPA Method 5 train and XAD-2 cartridges described in Appendix A.

Fugitive emissions released through the open cylinder door during charge changes appeared as a dense white plume which persisted throughout the sampling. Table 37 presents the qualitative organic analysis for these samples in concentration per volume of air sampled. It was not feasible to quantify a mass emission rate due to large fluctuations in ambient air dilution caused by changing wind speed and direction.

9.3 VACUUM VENT EXHAUST

Certain wood treating processes require the application of pressure and vacuum at various steps of the treating cycle. The pressure release and vacuum exhaust are sources of fugitive emissions, both aerosols and vapors.

Emissions from a vacuum vent common to the penta and creosote treating cylinders were characterized. The frequency of such emissions is variable but less than 10 percent of the treatment period. During the course of a single treating cycle at this facility, the chronological sequence in Table 38 was observed. Grab samples were analyzed onsite for total hydrocarbons (THC)

TABLE 36. CHARACTERIZATION OF PENTA AND CREOSOTE TREATING CYLINDER SPILLAGE AND DRIPPAGE

Sample location:	Penta treating cylinder spillage and drippage		Creosote treating cylinder spillage and drippage	
Date collected:	9/23/80	9/25/80	9/23/80	9/25/80
Compound	Concentrations in μg/g			
Pentachlorophenol	1,500	2,100	390	1,800
Phenol	<10	<10	<20	<10
Fluoranthene	29	180	420	200
Naphthalene	50	200	1,300	1,400
Benzo(a)anthracene	60	80	870	1,000
Benzo(a)pyrene	50	5.6	240	200
Benzofluoranthenes	54	26	700	500
Chrysene	50	85	710	850
Acenaphthylene	16	11	72	180
Anthracene	47	55	1,200	1,500
Benzo(g,h,i)perylene	<10	<5	<50	40
Fluorene	110	140	1,100	2,600
Phenanthrene	150	320	2,300	2,200
Dibenzo(a,h)anthracene	<10	<5	<50	20
Indeno(1,2,3-c,d)pyrene	<10	<5	<50	52
Pyrene	24	140	370	1,700
Benzene	<0.5	0.1	0.3	15
Toluene	<0.5	0.5	<0.2	<1
Ethylbenzene	<0.5	0.5	<0.2	<1

TABLE 37. QUALITATIVE ORGANIC ANALYSIS RESULTS FOR FUGITIVE EMISSIONS

Sample location:	Penta treating cylinder			Creosote treating cylinder
Run number:	1	2	3	1
Compound	Concentration*			
Pentachlorophenol	<0.02	8.1	2.6	0.63
Phenol	<0.02	1.62	<0.02	0.11
Fluoranthene	0.026	<0.16	0.019	0.94
Naphthalene	0.057	5.8	1.9	2.8
Benzo(a)anthracene	<0.02	<0.16	<0.02	0.01
Benzo(a)pyrene	<0.02	<0.16	<0.02	<0.01
Benzofluoranthenes	<0.02	<0.16	<0.02	<0.01
Chrysene	<0.02	<0.16	<0.02	0.01
Acenaphthylene	0.13	0.29	0.11	0.086
Anthracene	0.026	0.05	0.03	0.46
Benzo(g,h,i)perylene	<0.02	<0.81	<0.02	<0.01
Fluorene	<0.02	0.32	0.46	0.08
Phenanthrene	0.31	0.49	0.28	2.8
Dibenzo(a,h)anthracene	<0.02	<0.81	<0.12	<0.01
Indeno(1,2,3-c,d)pyrene	<0.02	<0.16	<0.02	<0.67

*Concentration units are mg/sm^3

TABLE 38. TREATING CYCLE SEQUENCE

Treating Cycle	Pressure or vacuum (atmosphere)	Temp. ^{o}F (^{o}C)	Time started	Time completed	Lapse time (hrs)
CONDITIONING					
1. Steaming					
2. Vacuum	23 in. (.77)		8:15 am	10:15 am	2.00
3. Preservative In.			5:45 am	6:15 am	.83
4. Heating in Oil		210 (99)	6:15 am	10:15 am	4.00
5. Preservative Back			10:15 am	10:45 am	.83
TREATING					
6. Initial Vacuum					
7. Initial Air	70 psi (4.8)		10:45 am	11:00 am	.42
8. Preservative In.			11:00 am	11:20 am	.55
9. Pressure Commenced	90 psi (6.1)	200 (93)	11:20 am	1:30 pm	2.28
10. Preservative Back		210 (99)	1:30 pm	2:00 pm	.83
11. Final Vacuum	23 in. (.77)		2:00 pm	4:00 pm	2.00
12. Recovering Drippings			4:00 pm	4:15 pm	.42
13. Secondary Steam					
14. Secondary Vacuum					
15. Changing Time					.42
			TOTAL TIME		11.0

TABLE 39. SUMMARY OF TOTAL HYDROCARBON DETERMINATIONS

Emission Point	Penta pan evaporation device	Creosote pan evaporation device	Penta treating cylinder fugitive emissions	Creosote treating cylinder fugitive emissions	Vacuum vent	
					Penta cycle	Creosote cycle
Date	ppm* total hydrocarbons as methane (time of day)**					
9/23/80	444 (1326)	—	—	—	—	—
9/24/80	—	892 (1730) 36 (1747)	3,660 (1326) 984 (1351) 1,790 (1425)	646 (1519)	—	—
9/25/80	165 (1250) 185 (1305)	1,460 (1450) 1,440 (1514)	—	221 (0828) 365 (0914)	42,100 (1034) 52,300 (1052)	22,100 (1332) 41,500 (1349)

*ppm = parts per million
**(time) = time sample was collected, 24-hr clock

TABLE 40. SUMMARY OF SPECIFIC LOW-MOLECULAR-WEIGHT HYDROCARBON DETERMINATIONS AT A COMMON VACUUM VENT

Date (Emission points)	Time (24-hr clock)	Benzene*	Toluene	Ethylbenzene	Sum of specific hydrocarbons as methane
(penta thermal evaporation device)					
9/23/80	1650	1.6	ND	ND	4.6
9/25/80	1250	ND	ND	ND	ND
	1305	ND	ND	1.8	6.9
(creosote thermal evaporation device)					
9/24/80	1730	ND	ND	ND	ND
	1747	ND	ND	1.5	5.8
9/25/80	1450	ND	ND	13	53
	1514	ND	ND	13	53
(penta treating cylinder fugitive emissions)					
9/24/80	1326	ND	ND	ND	ND
	1351	ND	ND	27	110
	1425	ND	ND	11	43
(creosote treating cylinder fugitive emissions)					
9/24/80	1519	ND	ND	ND	ND
2/25/80	828	ND	ND	3.3	13
	914	ND	ND	2.1	8.6
(vacuum vent during penta cycle)					
9/25/80	1034	ND	1,570	1,610	11,600
	1052	104	1,480	1,720	12,000
(vacuum vent during creosote cycle)					
9/25/80	1332	1,310	42	1,620	10,100
	1349	1,300	64	1,600	9,960

*Hydrocarbon units in ppm
ND = not detectable

using the procedures described in Appendix A. Table 39 presents a summary of the results of the THC analysis during both penta and creosote treating cycles.

Grab samples of emissions from the vacuum vent also were analyzed for specific low-molecular-weight hydrocarbons: benzene, toluene, and ethylbenzene. These components were measured onsite using the methods and procedures described in Appendix A. Table 39 presents a summary of the analyses for specific low-molecular-weight emissions during penta and creosote treating cycles. These data show that significant concentrations of organic compounds are emitted to the atmosphere.

From Table 38, it can be seen that a vacuum was drawn for a total of 4 hours, and the retort was open for a total of 50 minutes. Based on these emission periods and the data contained in Table 39, emission quantities can be calculated. Of these quantities, the vacuum vent represents the greatest emission source. A field estimated vacuum vent exhaust of 12.5 sm^3/min (see Appendix A) with an organic concentration of 42,000 ppm as methane -- Table 39 .042 x 16 x 273/22.4 x 298 = 0.027 g/l) results in an emission rate of 340 g/min. For a plant operating weekdays with two retorts emitting for a half hour per charge, the annual emission rate would be 5.3 metric ton per year. By comparison, a medium-sized oil refinery may emit fugitive VOC as much as 1,000 metric ton/year[8]. Therefore, though these concentrations of organics may cause localized problems, the total emission burden is small compared to some other sources.

9.4 SETTLED SOLID RESIDUES

The final disposal of residues that accumulates is treatment lagoons, holding ponds or tank depends on site specific management practices. When the equipment is part of the processing plant the accumulated material is frequently recycled if possible. Contrarily holding lagoons and spray ponds may only occasionally be cleaned or else residue may accumulate until the lagoon is bypassed for some alternative devise. In the latter case, residues may require removal to prevent impacting future land use. For the field sites surveyed plants A and C currently transfer residual sludge or ash to on-site landfills by direct hauling. Plant B's residue impacts the environment as a continuous minor land application is affected indirectly through lagoon bottom buildup. The character of this material is presented in Table 41. Plant A had a similar prior practice that was abandon for evaporation.

Without more samples than were analyzed no truly representative numbers are available to quantify the balance of materials between water and sediment. However, the high values of components in Table 41 indicate that incoming waste eventually decreases in concentration while the bottom sludge increases. As discussed in Section 6, higher molecular weight organics are not emitted very rapidly at low temperatures. Thus it is assumed that toxic organics are settled out of the wastewater onto the lagoon bottom and remain for some period of time. Residues are thereby slowly transferred to land albeit with undocumented environmental effects.

TABLE 41. LAGOON SETTLED SLUDGE COMPOSITION

Component	Plant B μg/g	Plant A (Abandon Pond) μg/g
Pentachlorophenol	15,000	
Phenol	<50	
Fluoroanthene	5,800	
Naphthalene	1,500	
Benzo(a)anthracene	2,600	
Chrysene	2,000	
Anthracene	1,700	
Fluorene	5,600	
Phenanthrene	9,000	
Pyrene	4,400	
Other PNAs	490	
CDD	2.1	2.2
CDF	1.4	0.4

REFERENCES

1. Environmental Protection Agency "Timber Products Processing Point Source Category Effluent Limitations Guidelines, Pretreatment Standards and New Source Performance Standards" 40 CFR Part 429 44 FR 62810-840 (October 31, 1979) and 46 FR 8260-295 (January 16, 1981).

2. DaRos, B. et al., "Wood Preserving Industry Multimedia Emission Inventory" EPA 600/2-81-066 (In press).

3. Thibodeaux, L. J. "A Test Method for Volatile Component Stripping of Waste Water" EPA-660/2-74-044 (May 1974).

4. Thibodeaux, L. J. et al., "Measurement of Volatile Chemical Emissions from Wastewater Basins" EPA IERL (draft).

5. McAlister, J. A., B. G. Turner and R. B. Estridge "Treatment of Selected Internal Kraft Mill Wastes in a Cooling Tower" EPA-12040 EEK (August 1971).

6. Harris, J. C. et al., "Dioxin Emissions from Combustion Sources: A Review of the Current State of Knowledge" A. D. Little Inc. report to ASME, Cambridge, MA, December 29, 1980.

7. Esposito, M. P., T. O. Tiernan and F. E. Dryden, "Dioxins" EPA-600/2-80-197 (November 1980).

8. Radian Corp: "Control Techniques for Volatile Organic Emissions from Stationary Sources" EPA-450/2-78-002 (May 1978).

APPENDIX A

CHARACTERIZATION OF MULTIMEDIA EMISSIONS FROM THERMAL (PAN) EVAPORATION OF WOOD PRESERVING WASTEWATERS

Raw data for this study has been compiled and is available upon request. That data covers the source emission sampling for high-molecular-weight, and total hydrocarbon, and specific low-molecular-weight determinations. Copies may be obtained from EPA-Industrial Environmental Research Laboratory, 26 W. St. Clair Street, Cincinnati, OH.

A.1 TEST SITE

The wood treating facility tested is decribed in Section 5 with a schematic of the plant wastewater/preservative recovery system shown in Figure 1. The treated product amounted (17,320 ft^3) 490m^3 to during the July 22 to 25, 1980 field test period. Table A-1 presents a summary of the production components during the field test.

A.2 FIELD TEST PROGRAM

The following subsections describe the equipment and techniques employed during sampling.

TABLE A-1. SUMMARY OF TREATING PRODUCTION FOR THE PERIOD JULY 22 THROUGH JULY 25, 1980

Treated Product	5Δ Penta Light Oil		Creosote	
	m^3	ft^3	m^3	ft^3
Utility poles	42.6	1,509		
Posts	113.6	4,012		
Lumber	118.4	4,180	178.9	6,318
Pilings			37.0	1,306
Total	274.7	9,701	215.9	7,624

A.2.1 Source Emission Sampling of Pan Evaporation Devices

Sampling of high-molecular-weight organic emissions from the pan evaporator outlet was conducted using the EPA Method 5 sampling train nonisokinetically as shown in Figure A-1. The train consisted of a heated 1/2-inch O.D. Teflon sample line connected to an empty Greenberg-Smith impinger (without an impaction plate), followed by the XAD-2 resin cartridge. The resin was followed by a second Greenberg-Smith impinger containing 100 ml of deionized water. The third impinger, an empty Greenberg-Smith without an impaction plate, was followed by a silica gel desiccant (SiO_2) trap to protect the vacuum pump and sampling control module from moisture.

Four complete source tests were conducted at the penta (pan) thermal evaporator and at the creosote thermal (pan) evaporator. The evaporators and sampling locations are shown in Figures A-2 and A-3. For each source test, the sampling equipment was placed on the roof of the thermal (pan) evaporator, the Teflon sampling line was allowed to preheat to approximately 250°F, and the impinger train was prepared. Sampling was started by turning on the vacuum pump and opening the coarse adjusting valve to its midpoint. This valve position was maintained during the entire sampling period.

The volume of condensate determined the possible sampling times. As the first impinger filled with water, control of the sampling rate was lost. The sampling run was terminated by shutting off the vacuum pump, disconnecting and sealing the inlet and outlet of the Teflon sample line, and moving the train to the field laboratory. Table A-2 presents a summary of the pertinent source sampling parameters at each test location.

Samples were transferred from the sample trains to specially cleaned and labeled storage containers. The probe nozzle, probe, and connecting lines were rinsed with methylene chloride, and the recovered samples transferred to the appropriate storage containers. Immediately following sample recovery, all samples were iced in the field and maintained under those conditions for their transport to the analytical laboratory.

A.2.2 Source Emission Sampling of Penta and Creosote Treating Cylinders

Sampling of high-molecular-weight emissions during the unloading and charging of the penta and creosote treating cylinders was conducted using the same procedures and methods described in section A.2.1. The sampling locations are shown in Figures A-4 and A-5. Sampling was initiated a few minutes prior to opening the cylinder door and terminated a few minutes after the door was closed. Sampling times varied from 11 to 21 min and were dependent upon the size of the charge being unloaded or loaded and the ease with which the operation proceeded. Table A-3 presents a summary of the pertinent source sampling parameters for each test.

A.2.3 Total Hydrocarbon Determinations

Total hydrocarbon sampling was conducted at the outlet of the penta and creosote thermal (pan) evaporators, the penta and creosote treating cylinders

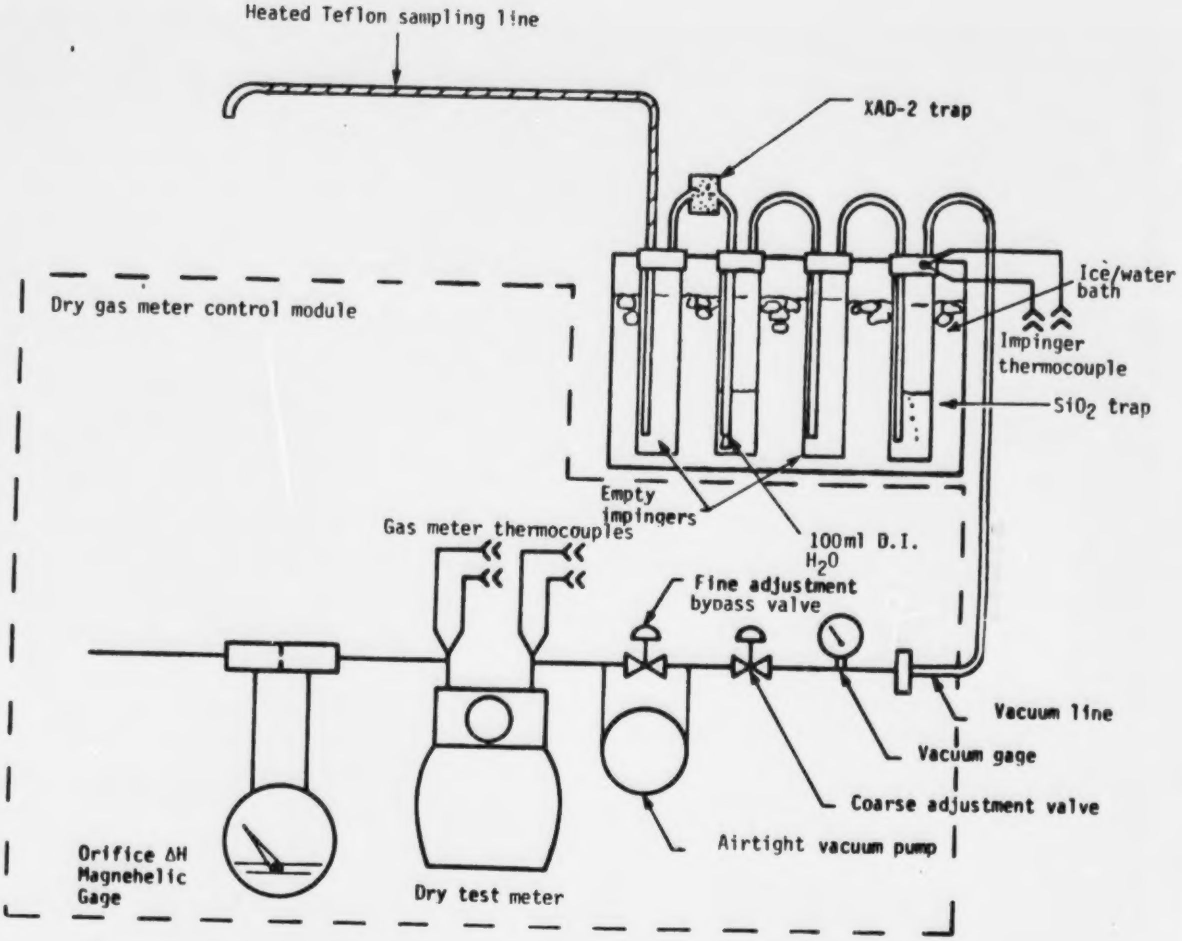

Heated Teflon sampling line
XAD-2 trap
Ice/water bath
Impinger thermocouple
SiO_2 trap
Dry gas meter control module
Empty impingers
100ml D.I. H_2O
Gas meter thermocouples
Fine adjustment bypass valve
Vacuum line
Vacuum gage
Coarse adjustment valve
Airtight vacuum pump
Orifice ΔH Magnehelic Gage
Dry test meter

Figure A-1. Schematic of modified EPA Method 5 sampling train.

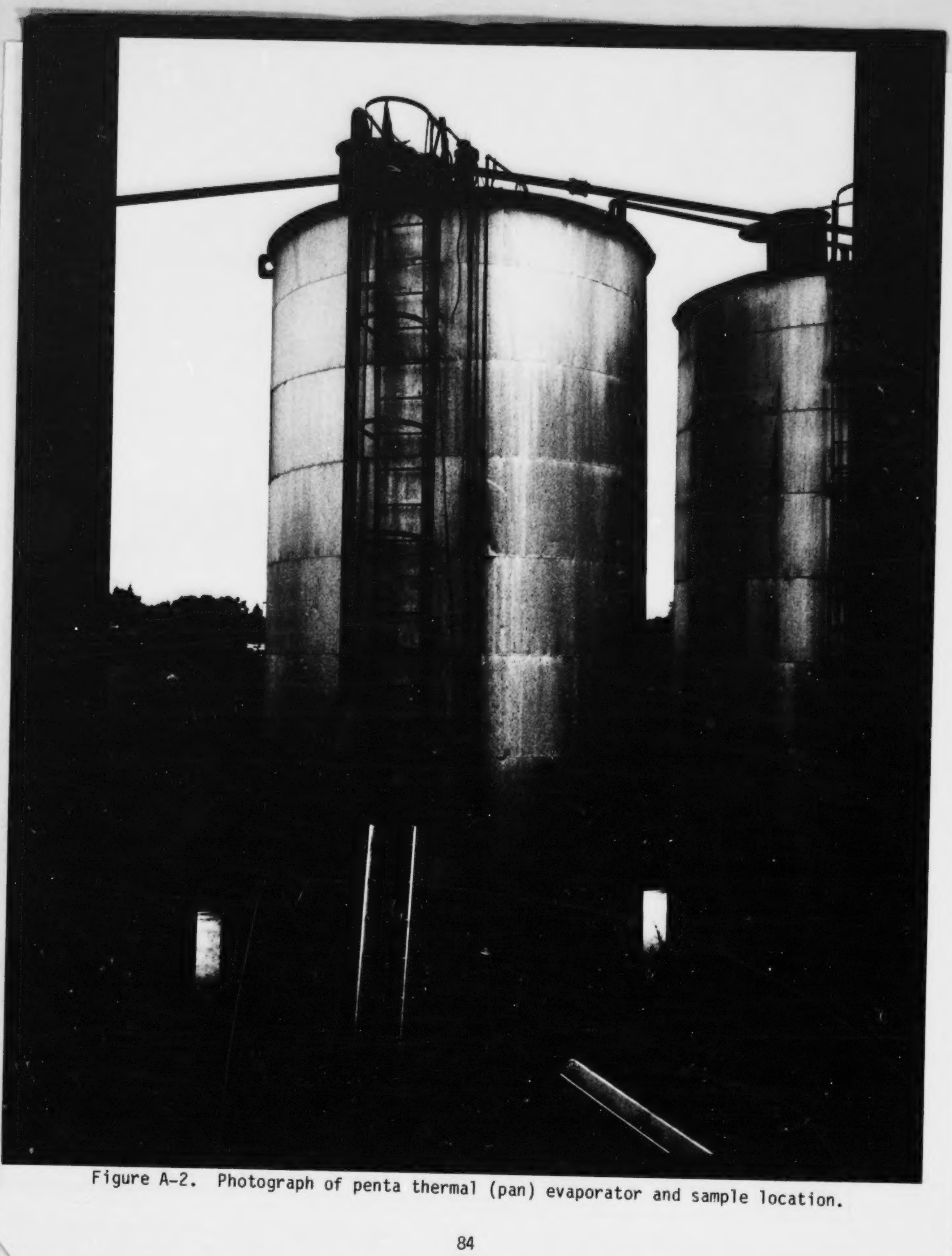


Figure A-2. Photograph of penta thermal (pan) evaporator and sample location.

Figure A-3. Photograph of creosote thermal (pan) evaporator.

TABLE A-2. SUMMARY OF SOURCE EMISSION SAMPLING PARAMETERS FOR TEST CONDUCTED AT THE PENTA AND CREOSOTE THERMAL (PAN) EVAPORATION DEVICES

Location/ Run Number	Date	Barometric Pressure (inches) (Hg)	Actual Sample Volume (acfm)	Meter Temperature (°F)	Condensate Volume (ml)	Stack Temperature (°F)	Molecular[a] Weight Dry (lb/lb-mole)	Molecular Weight Wet (lb/lb-mole)	Sampled Gas Volume (scfm)	Δ H_2O	Total Sampling Time (min)
Penta Evap 1	9-24-80	29.2	18.90	59.0	679	209	29.84	22.43	19.08	62.6	50.0
	9-24-80	29.2	0.695	63.5	1,300	215	29.84	18.13	0.697	98.9	29.0
	9-25-80	29.4	19.5	48.5	972	209	29.84	20.036	6.50	82.8	19.5
	9-26-80	29.5	8.67	54.8	598	206	29.84	20.82	8.8	76.2	15.0
Creosote Evap 1	9-24-80	29.4	16.06	59.3	622	191	29.84	22.38	17.16	63.1	30.0
	9-24-80	29.2	27.29	59.0	1,130	193	29.84	22.1	29.02	64.7	56.0
	9-25-80	29.4	22.00	49.7	762	190	29.84	22.72	23.87	60.1	45.0
	9-25-80	29.5	19.41	55.5	945	195	29.84	27.78	20.89	68.1	43.5

[a] Assumed MW of air.

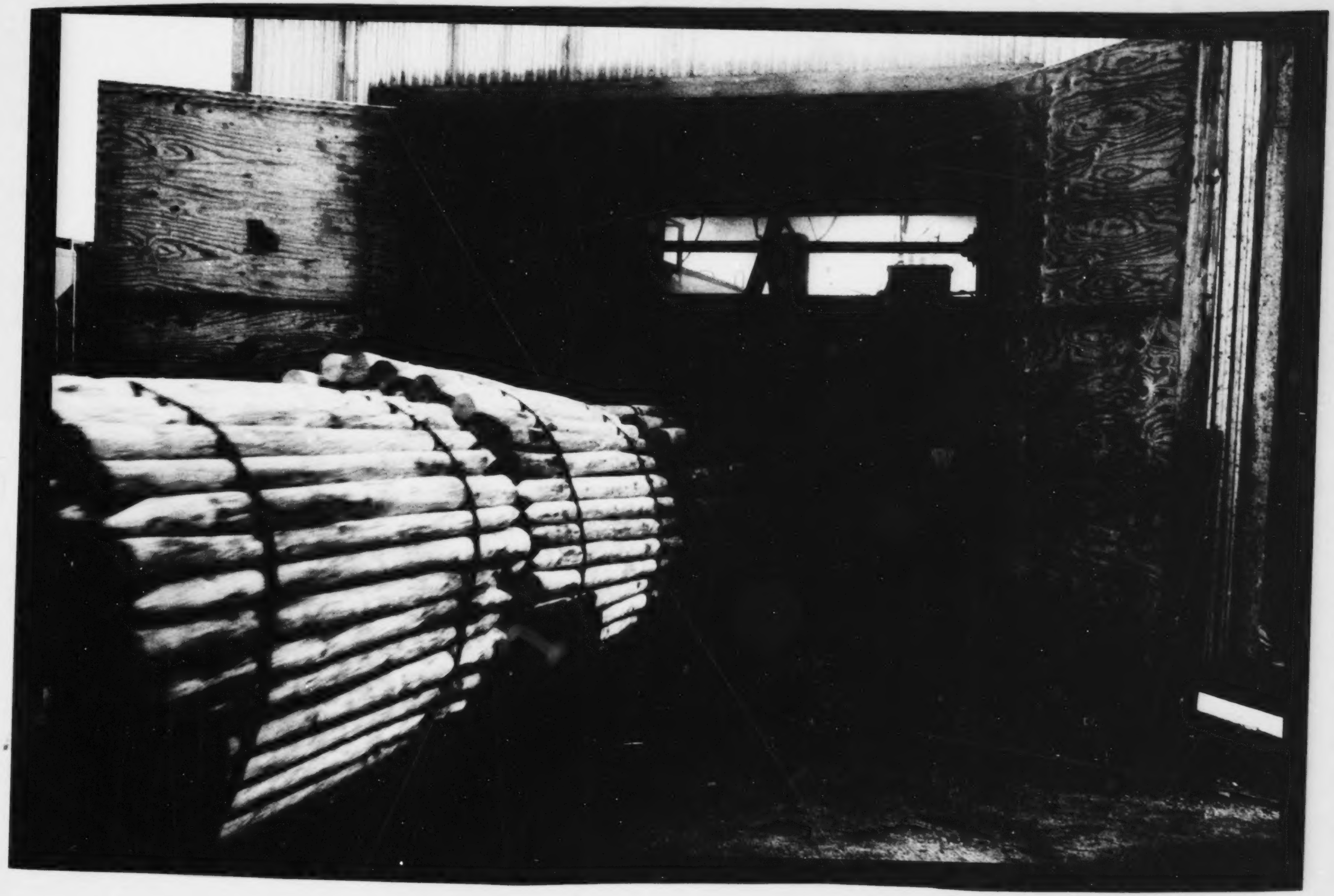


Figure A-4. Photograph of penta treating cylinder being charged with poles and the fugitive emission vent.

Figure A-5. Photograph of creosote treating cylinder building and fugitive emissions vent.

TABLE A-3. SUMMARY OF SOURCE EMISSION SAMPLING PARAMETERS FOR TESTS CONDUCTED AT THE PENTA AND CREOSOTE TREATING CYLINDER DURING UNLOADING AND CHARGING OPERATIONS

Location/ Run Number	Date	Barometric pressure (inches) (Hg)	Actual* sample volume (acfm)	Meter temperature (°F)	Condensate volume (ml)	Stack temperature (°F)	Molecular[a] weight dry (lb/lb-mole)	Molecular weight wet (lb/lb-mole)	Sampled gas volume (scfm)	Percent H_2O	Total sampling time (min)
PEP Retort											
1	9-23-80	29.45	16.49	73.0	55.5	82.0	29.84	28.19	16.17	13.9	11.0
2	9-24-80	29.24	21.85	61.5	29.7	90.0	29.84	29.12	21.73	6.04	14.0
3	9-25-80	29.40	22.39	52.0	5.1	69.0	29.84	29.72	22.81	1.0	15.0
Creosote Retort 1	9-26-80	29.40	24.5	43.0	--	70.0	29.84	29.84	25.17	0.0	21.0

*Cubic feet per minute

during unloading and loading, and at the outlet of the vacuum vent discharge to the barometric condenser. Sampling was conducted using the system shown in Figure A-6. The gas sample was extracted from the stack via a 7μ sintered, stainless steel Model No. SS-4 FE-7 filter, manufactured by Nupro Valve Company, Willoughby, Ohio. The filter removed fine particulates which could, if allowed to pass into the THC analyzer, occlude the FID sample inlet capillary. A 0.006m O.D. stainless steel probe connected the filter unit to the heated sampling line via a three-way stainless steel solenoid valve. This valve introduced sample gas or calibration gas depending on the desired mode of operation. A 100-ft, heat-traced, 3/8-inch O.D. Teflon sample line manufactured by Unitherm Company was used to transport the sample to the vacuum pump. The sample line temperature was maintained at 394°K by internal temperature controllers already installed. A Teflon-coated diaphragm vacuum pump manufactured by Thomas Industries, Sheboygan, Wisconsin, was used to pull the sample through the heated line. From the vacuum pump exit, the sample was split and routed to the analyzers via short lengths of heated Teflon line.

Prior to operation and calibration, the completed sampling system was operated at normal line sampling conditions and purged for several hours with zero grade nitrogen to remove any traces of residual hydrocarbon contamination in the lines. During this "bake-out" procedure, stainless steel tube unions, filters and probes were heated using a propane torch. Before and after each test, a leak test was performed on the sampling system followed by calibration of the THC analyzer using zero grade nitrogen gas and a mixture of 801 ppm methane in nitrogen. During calibration, the three-way valve was positioned to block the sample probe and filter, allowing the calibration gas to pass into the heat-traced sample line. Introducing the calibration gases at this location, ensured the sample gases and calibration gases were treated in the same manner, nullifying possible undesirable effects due to absorption in the sampling line and system.

A model 400 total hydrocarbon (THC) analyzer, manufactured by Beckman Instruments, Fullerton, California, was used to continuously monitor total hydrocarbon emissions from the vacuum vent discharge. This analyzer uses the flame ionization detection (FID) method. The analyzer output was recorded using a Model 585 strip chart recorder manufactured by Linear Instruments Corporation, Irvine, California.

The FID was operated using zero grade (<1.0 HC) hydrogen fuel and zero grade air supplied by Airco Industrial Gases, Santa Clara, California. Hydrogen fuel and zero air pressure were set at 207 KPa (30 psi) and 103 KPa (15 psi), respectively, using internal differential pressure regulators in the analyzer.

After approximately 1 hour of sampling at the vacuum vent, the heated sampling line was heavily contaminated with hydrocarbons. Attempts to recalibrate and rezero the THC analyzer were impossible. At this point, the heated bulb method was substituted for the continuous method.

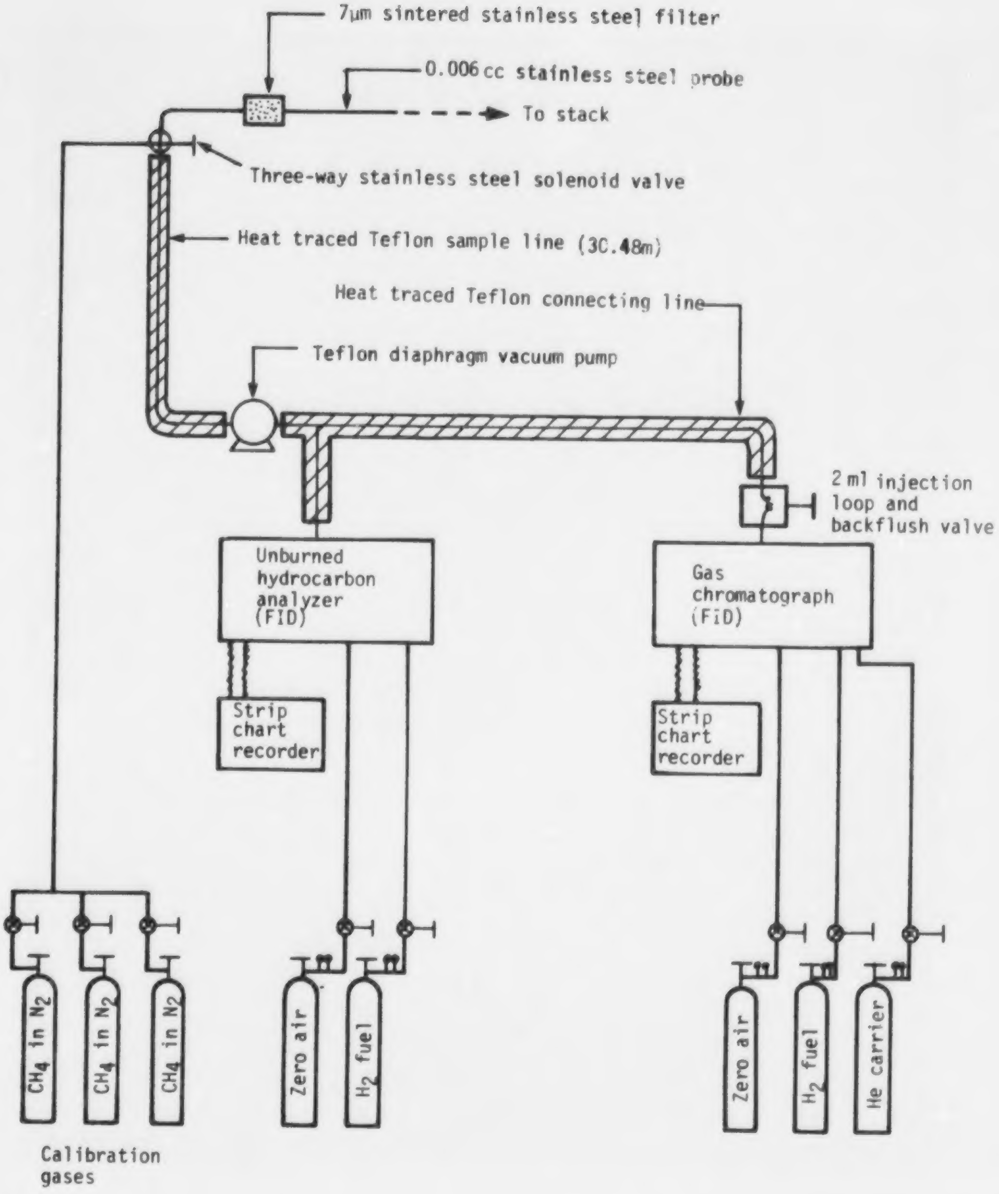

7μm sintered stainless steel filter
0.006 cc stainless steel probe
To stack
Three-way stainless steel solenoid valve
Heat traced Teflon sample line (30.48m)
Heat traced Teflon connecting line
Teflon diaphragm vacuum pump
2 ml injection loop and backflush valve
Unburned hydrocarbon analyzer (FID)
Gas chromatograph (FID)
Strip chart recorder
Strip chart recorder
CH_4 in N_2
CH_4 in N_2
CH_4 in N_2
Zero air
H_2 fuel
Zero air
H_2 fuel
He carrier
Calibration gases

Figure A-6. Schematic of unburned hydrocarbon and gas chromatograph sampling system.

Grab samples from the appropriate source were collected by evacuating and purging 250-ml pyrex glass sampling bulbs heated to 121°C (250°F). Aliquotes of the collected samples then were withdrawn from the heated bulb using a 5-ml gas-tight syringe inserted through a septum port in the bulb. The syringe contents were injected via a 2-cm^3 injection loop and backflush valve into a Varian Model 3700 gas chromatograph (GC). GC operating conditions for THC analysis are presented in Table A-4.

Table 39 presents a summary of the results of THC determinations at the various emission points based on the total area chromatograph and backflush. The results are reported as PPM methane (CH_4).

The accuracy of the data presented using the heated bulb method of sampling varies substantially. The greatest error associated with this method is sample integrity. It was apparent that samples collected at the penta and creosote thermal (pan) evaporators were mostly water vapor. When these samples were transferred via syringe to the GC for analysis, condensation within the syringe most likely co-condensed hydrocarbons, thus causing lower values than would be expected. The error is estimated to be ± 50 percent maximum.

THC values for samples collected from the treating cylinders are also very uncertain due to the nature of the sampling site. The fugitive emissions were prone to large fluctuations in ambient air dilution caused by changing wind speed and direction. The possible error associated with these sites, and based on total gas volumes, is estimated to be +100 to 50 percent. The error based on water vapor volume will be much lower.

THC values for samples collected from the vacuum vent have less uncertainty about them since emissions were relatively low in moisture content. It is estimated that the error associated with these values is ±20 percent.

A.2.4 Specific Low-Molecular-Weight Hydrocarbon Determinations

Periodically, benzene, toluene and ethylbenzene concentrations were determined for each emission point. The Varian Model 3700 gas chromatograph separated the hydrocarbon sample into its components. GC operating conditions for the analysis were the same as presented in Table A-4.

Calibration standards for the compounds of interest were prepared onsite using 50-liter Teflon bags and the methods outlined in "Evaluation of Emission Test Methods for Halogenated Hydrocarbons," Vol. I, EPA-600/4-79-025, March 1979. The calibration mixture was then used to calibrate the GC and to give retention indices for the appropriate components. Table 39 presents a summary of the resultant analysis. The data are reported by ppm (specific specie) and as ppm methane.

TABLE A-4. GAS CHROMATOGRAPH OPERATING CONDITIONS FOR THE DETERMINATION OF TOTAL HYDROCARBONS

Column:	6-ft x 1/8-inch O.D. stainless steel tubing packed with 1 percent SP 1000 on carbopack (80/100 mesh)
Injector temperature:	120°C
Temperature program:	Isothermal at 120°C
Special note:	Inject 2 cm^3 sample for approximately 5 min or until ethyl benzene component was eluted, then back-flush until baseline returned to zero.

A.2.5 Liquid Grab Sampling

Grab samples of the following were collected during the 3-day sampling period:

- Penta thermal (pan) evaporator contents
- Creosote thermal (pan) evaporator contents
- Bulk penta in treating oil (before use)
- Bulk creosote (before use)
- Penta treating cylinder spillage
- Creosote treating cylinder spillage
- Penta oil/water separator (both fractions)
- Creosote oil/water separator (both fractions)

Liquid samples of the penta and creosote evaporator contents were collected in the morning and afternoon of each sampling day. Samples were collected by lowering a precleaned sample container into the evaporator tank and retrieving the liquid near the surface.

Samples of liquid fractions contained in the penta and creosote primary oil/water separators were obtained on a daily basis. Samples were obtained by immersing an inverted sample container into the appropriate layer then tipping it to collect the sample. Some contamination was observed during retrieval of the lower fraction; however, this was minimal with respect to the initial sample volume. This will bias the creosote wastewater values to the high side, and the penta recycle oil to the low side.

The remaining samples of bulk penta and creosote, and the penta and creosote treating cylinder spillage, were collected on a one-time basis. After collection, all samples were immediately iced and maintained on ice for transport to the analytical laboratory.

A.3 ANALYTICAL METHODS

Samples from the thermal (pan) evaporation system were received on October 21, 1980. The samples were assigned consecutive laboratory identification numbers and stored at 4°C until analyzed.

A.3.1 Analytical Methods

Analyses were conducted for volatile organics, semivolatile organics, and dioxins. Volatile organics analyses were based on variations to EPA Method 624. Semivolatile organic (phenols and polynuclear aromatics) analyses were based on sample preparation variation to EPA Method 625 in conjunction with fused silica capillary column gas chromatography/mass spectrometry (GC/MS).

Analysis of Volatile Organics--

The analytes of interest were benzene, toluene, and ethylbenzene. The sludge and wastewater samples were analyzed for these components.

A 1.0g aliquot of the mixed sludge or wastewater was weighed into a 15-ml crimp top vial. Pentane (9 ml) and 1-bromo-2-chloropropane (10μg) were added as internal standards. A 1-μl aliquot of this diluted sample was injected in a 0.2 percent Carbowax 1500 on a Carbopack C packed GC column in a Finnegan 1020 GC/MS instrument. Analysis and quantitation were conducted per EPA Method 624 using the internal stnadard method.

Quality control for the volatiles analysis entailed the anlysis of method blanks and method standards spiked at 10 μg/g of sludge. In addition, the control requirements of Method 624, including instrument tuning to meet specifications, were met.

Analysis of Semivolatile Organics --

Semivolatile organics analyzed are listed in Table A-5. These analyses were conducted by variations to EPA Method 625. The variations were in the sample preparation and in the use of fused silica capillary column GC/MS to determine these compounds.

Sample Preparation --

Sludge samples were prepared as follows:

1. Place 10.0 g of the sludge in a clean 250-ml brown bottle. Add 10.0 g of anhydrous sodium sulfate and 100 ml of pesticide grade dichlormethane. Shake occasionally and allow to sit overnight at room temperature.

2. Take 1.0 ml of each extract for GC/FID screening. Store the remaining extract at 4°C.

3. As required by the GC/FID screening, filter the extract into a Kuderna-Danish concentrator and concetrate to 1.0 ml.

The GC/FID screening stage was necessitated by the wide variability of sample concentrations. Figure A-7 summarizes the semivolatile scheme for sludge samples.

The XAD-2 cartridge was carefully opened, any silicone stopcock grease removed with a CH_2Cl_2 wetted towel, and the contents transferred to a preextracted Soxhlet thimble. The XAD-2 material in the Soxhlet was spike with surrogate mix and extracted overnight with CH_2Cl_2.

To assure analysis of all organics collected during the XAD-2 sampling, two other samples were taken for each sampling train: a dichloromethane probe rinse and an impinger catch. For analysis, the dichloromethane rinse was added to the XAD-2 soxhlet extractor. The impinger water was acidified to

TABLE A-5. SEMIVOLATILE ORGANICS ANALYZED IN WOOD PRESERVING SAMPLES

Number	Name
1	Phenol
2	2-Nitrophenol
3	2,4 Dichlorophenol
4	2,4,6 Trichlorophenol
5	4-Nitrophenol
6	4,6-Dinitro-o-cresol
7	Pentachlorophenol
8	Acenaphthalene
9	Fluoranthene
10	Naphthalene
11	Benz(a)anthracene
12	Chrysene
13	Acenaphthylene
14	Phenanthrene
15	Fluorene
16	Pyrene
17	Benzofluoranthenes
18	Benzo(a)pyrene

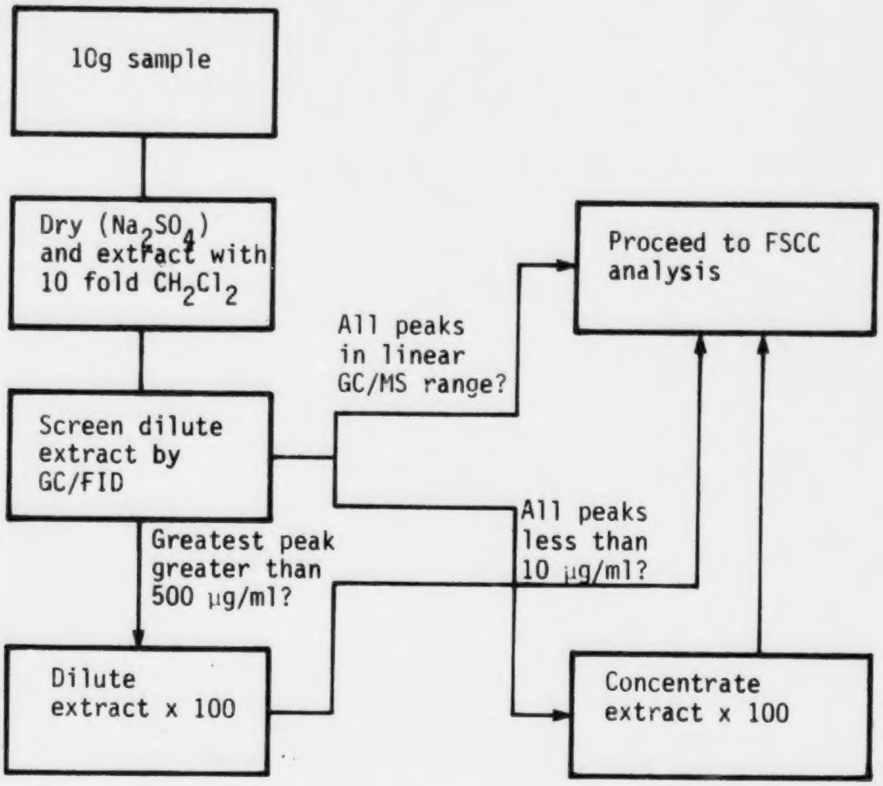

10g sample
Dry (Na_2SO_4) and extract with 10 fold CH_2Cl_2
Screen dilute extract by GC/FID
Greatest peak greater than 500 μg/ml?
Dilute extract x 100
All peaks in linear GC/MS range?
Proceed to FSCC analysis
All peaks less than 10 μg/ml?
Concentrate extract x 100

Figure A-7. Analysis scheme for phenols/PAHs in wood preserving sludges.

pH 1 with 6N H_2SO_4 and extracted overnight in a continuous liquid-liquid extractor. The water extract and XAD-2 extract were then combined, dried with anhydrous sodium sulfate, and concentrated to 1.0 ml.

Quality control for XAD-2 samples consisted of the analysis of surrogate spikes, field blanks, and spiked method blanks.

Extract Analysis --

Each of the extracts obtained as described in the previous section was analyzed for the compounds listed in Table A-5 using fused silica capillary column GC/MS. The instrument operating conditions also are listed in Table A-6.

The quality control requirements listed in EPA Method 625 were followed, including analytical calibration, mass spectrometer tuning to meet decafluorotriphenylphosphine (DFTPP) criteria, and the use of multiple intenal quantitation. The internal standards used were d_8-naphthalene, d_{10}-anthracene, and d_{12}-chrysene.

A.3.2 Analytical Results and Discussion

Volatile Organics--

Volatile organics (benzene, toluene, ethylbenzene) were determined in water and sludge samples using a pentane extraction method followed by GC/MS. Figure A-8 is a chromatogram of a method blank spiked with the compounds of interest at 1 μg/g. The solvent contaminants did not interface with the detemination of the compounds of interest.

Figure A-9 is a chromatogram from the analysis of a retort drip sample. This sample is typical, having very low or no detectable volatile aromatics. No contamination was detected in the analysis of method blanks. It was, however, necessary to increase the column bake cycle time after the injection of several samples because higher-molecular-weightr creosote components accumulated on the column and performance deteriorated without the extra bake cycle.

Semivolatile Organics--

Phenols and polynuclear aromatics were determined by solvent extraction and fused silica capillary column GC/MS. An extract prescreening procedure using GC with FID determined the appropriate extract concentration factors prior to GC/MS analysis. The prescreening was especially important with certain sample types (oil/water separator samples) which were extremely variable in content.

Two cases of contamination were detected during the course of the study. The XAD-2 blanks contained 10 to 200 μg of naphthalene. This is an XAD-2 contaminant as received from the manufacturing process and indicates an insufficient washing process prior to field sampling. Ony trace levels of other analytes (1 to 5 μg) were detected on the XAD-2. During the GC/MS injection of a series of thick creosote extracts, a serious cross-contamination was detected. As much as 0.1 percent sample-to-sample

TABLE A-6. FUSED SILICA CAPILLARY COLUMN PARAMETERS

Column:	
30m x 0.25 m SE-54 WCOT (J&W Scientific)	
Splitless Injection Parameters:	
Injection mode:	Splitless
Sweep initiation:	30 sec
Sweep flow:	Greater than or equal to 12 ml/min
Column flow (He) measured at atmospheric:	1.0 ml/min
Interface:	
Temperature:	300°C
Column directly coupled to source (no transfer lines)	
Temperature Program:	
Initial:	30°C for 2 min
Program:	Ramp to 300°C @ 10°C/min
Hold:	300°C, 15 min
Mass Spectral Parameters:	
Ionization mode/ energy:	Electron impact/70 eV
Total scan time:	1.0 sec
Mass range:	35 to 475 AMU

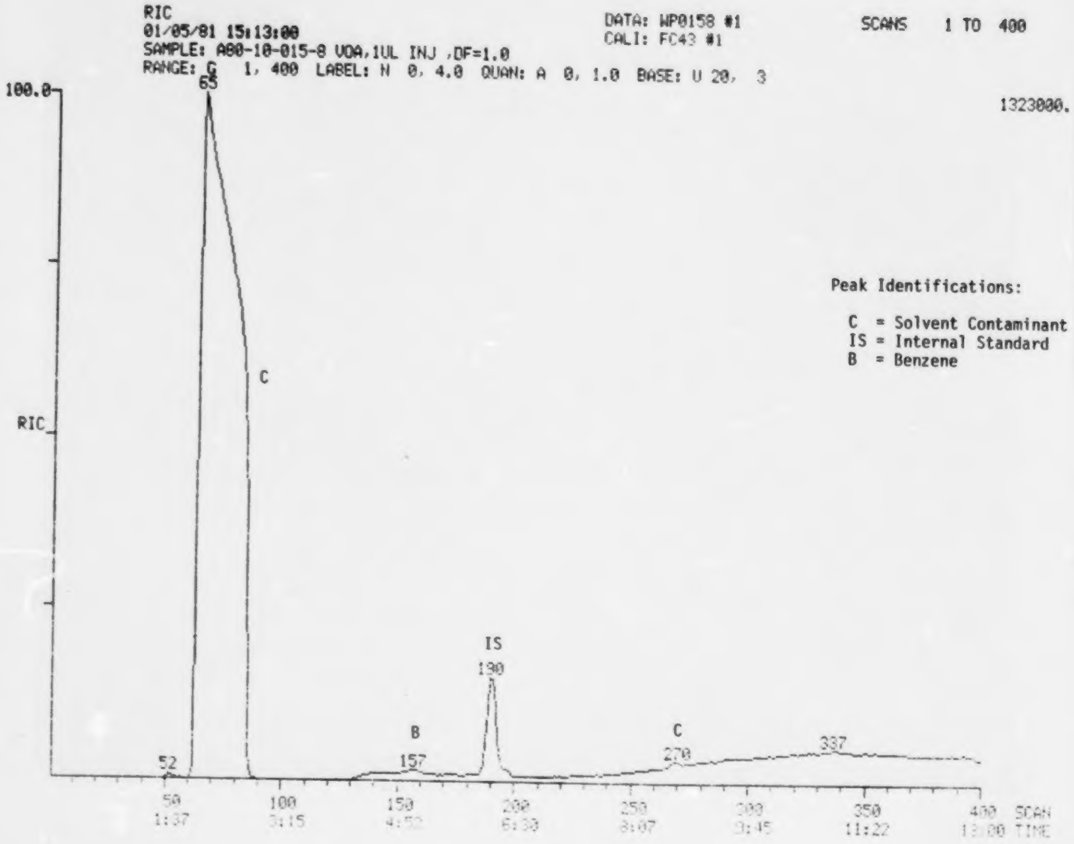


Figure A-8. Total ion current chromatogram of a volatiles standard.

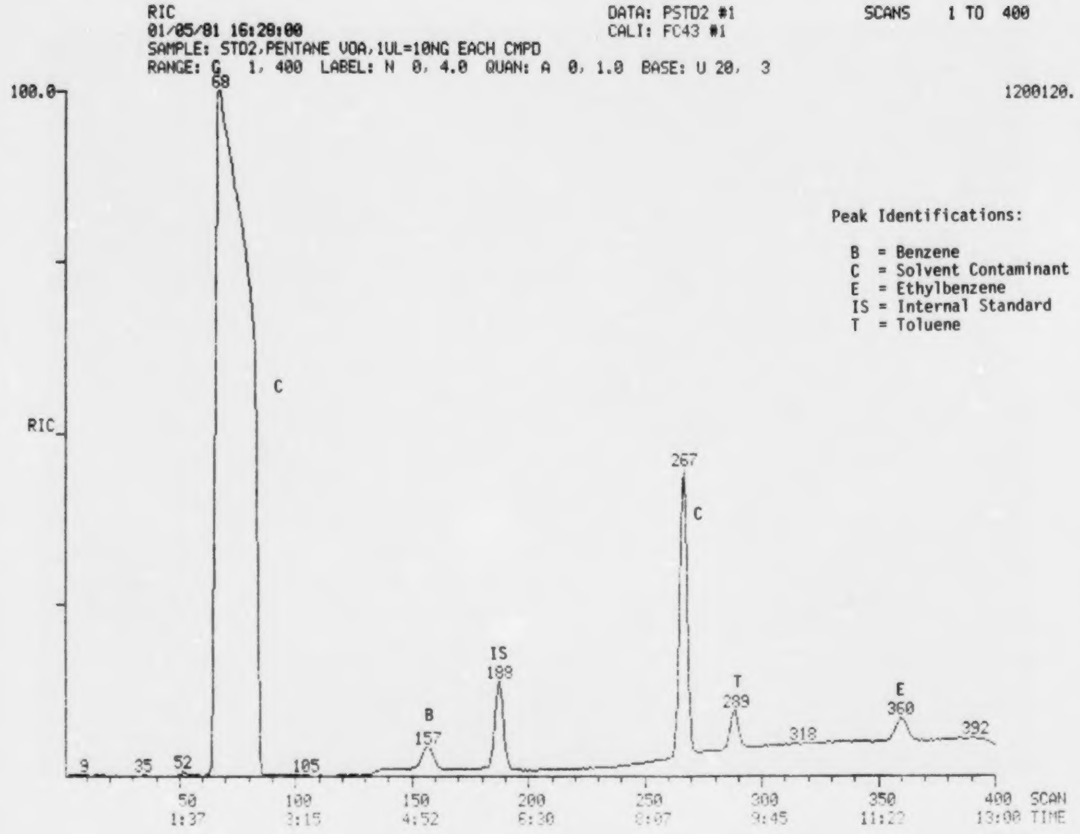


Figure A-9. Total ion current chromatogram for a retort drip volatiles analysis.

contamination was detected when using 1-µl capillary syringes. No method for routine cleaning of these syringes could be found. However, no such problem was detected with standard 10-µl syringes.

In the dirtiest creosote samples, the overall retention time of many compounds varied from that measured in the standards. However, the retention time relative to a nearby eluting internal standard was a reliable indentification criterion. Special care was needed with the benzo(a)pyrene isomers. Figure A-10 shows the M/E 126 and 252 exracted ion current profiles for one of the creosote samples. Although standards were not available, the other isomers were tentatively identified as listed. The two benzofluoranthenes could not be reliably separated in the presence of so many other compounds. It was decided to report these two as a single value for all samples.

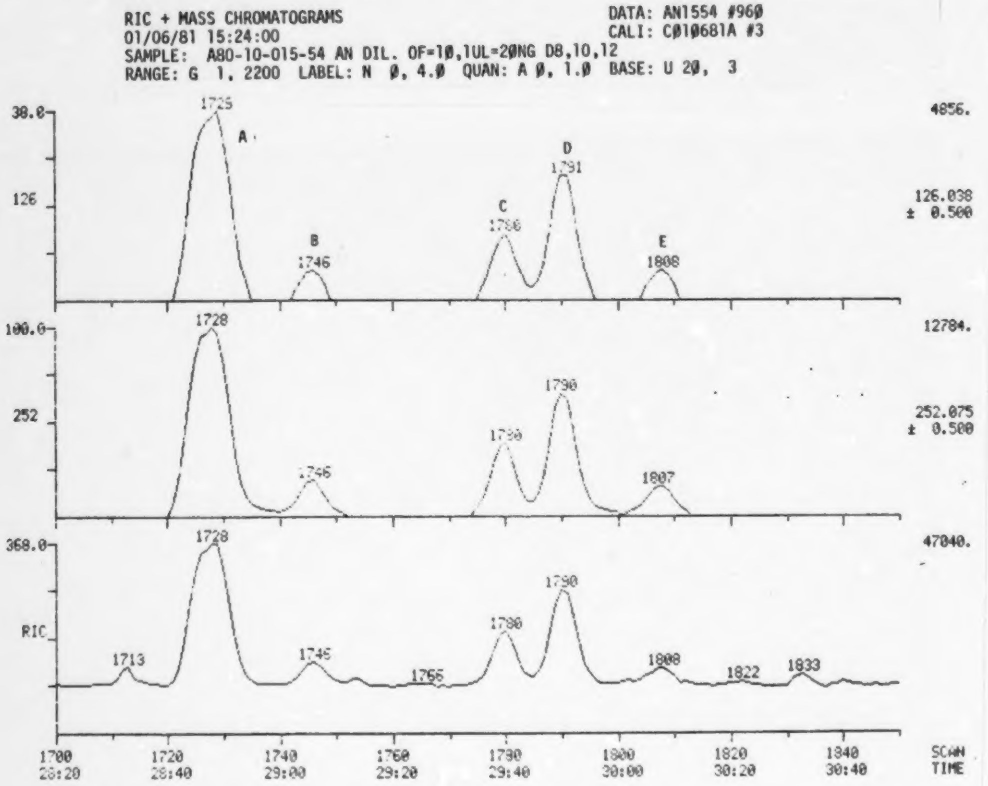
Figure A-11 shows the chromatograms from various spots in the creosote preserving process. A few of the major peaks are identified in each chromatogram. The creosote at this plant appears to be different from other creosotes in that the phenol content is very low (400 ppm).

Table A-7 presents a log of all samples collected, followed by Tables A-8 through A-21 which present the analytical data.

Figure A-12 shows samples from the pan evaporation process. It is clear that the liquid left behind in the evaporator is concentrated in the high-molecular-weight polynuclear species such as chrysene and benzo(a)pyrene. These polynuclears do not volatize to the same extent as the low-molecular-weight species. Figure A-12(d) is a chromatogram of an XAD-2 blank extract. Of the compounds of interest, only naphthalene was detected in the blank. Duplicate blank samples showed 100 and 140 µg of naphthalene. The XAD-2 cartridge extract shown in (d) is an 8,000-fold dilution of the total extract. The quantitative result for this sample wa 2.8g of naphthalene for the 10g sample.

Chromatograms for penta process samples are shown in Figure A-13. The use of petroleum distillate as the penta vehicle complicates the chromatograms immensely, since it also contains polynuclear aromatic hydrocarbons. The concentration of penta in these samples, however, was sufficiently high for reliable quantitation in the presence of the oil matrix. For lower concentations than seen here, an additional sample preparation of neutrals from acids would be necessary.

Figure A-14 shows chromatograms from the penta wastewater evaporation process. Penta was detected in the XAD-2 cartridge. However, the hydrocarbons appear to the preferentially evaporated as evidenced by the concentration of penta in the pan bottoms. No contamination from penta was seen in XAD-2 blanks.

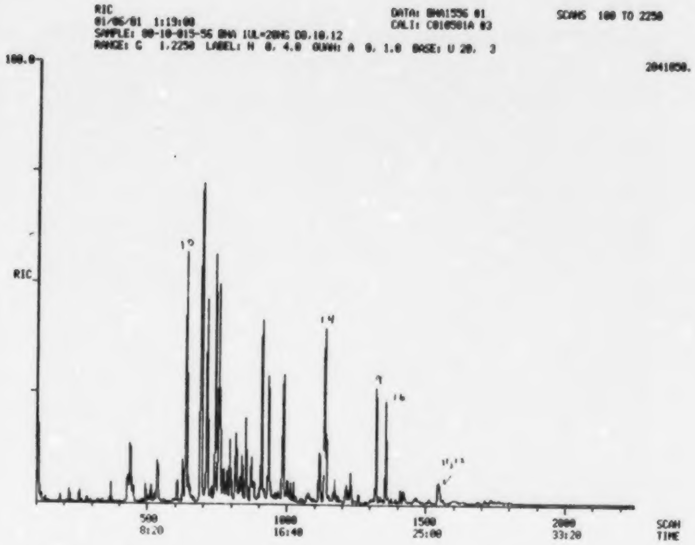


RIC + MASS CHROMATOGRAMS
01/06/81 15:24:00
SAMPLE: A80-10-015-54 AN DIL. OF=10,1UL=20NG D8,10,12
RANGE: G 1, 2200 LABEL: N 0, 4.0 QUAN: A 0, 1.0 BASE: U 20, 3

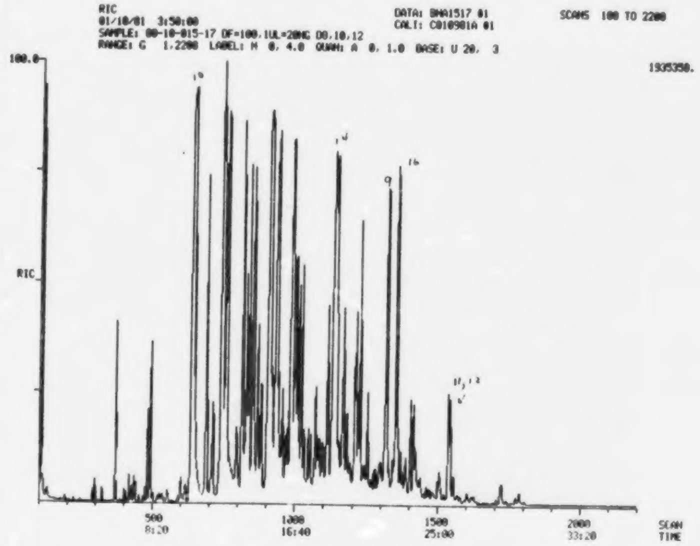
DATA: AN1554 #960
CALI: C010681A #3

NOTE: Peak A is unresolved benzo (b+k) fluoranthenes.
Peak D is benzo(a)pyrene. Peaks B, C, and E are tentatively indentified as benzo(j)fluoranthene, benzo(e)pyrene, and perylene.

Figure A-10. M/E 126, 252, and RIC for the benzo(a)pyrene region of a creosote extract FSCC analysis.

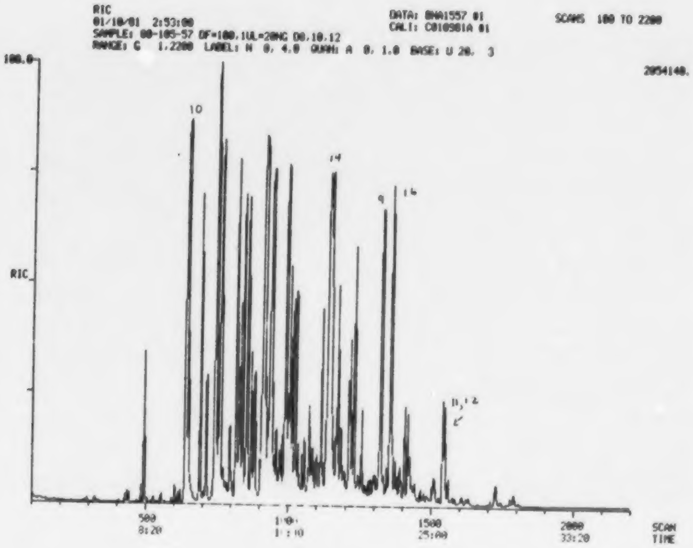


(a) Creosote oil/water separator -- top layer

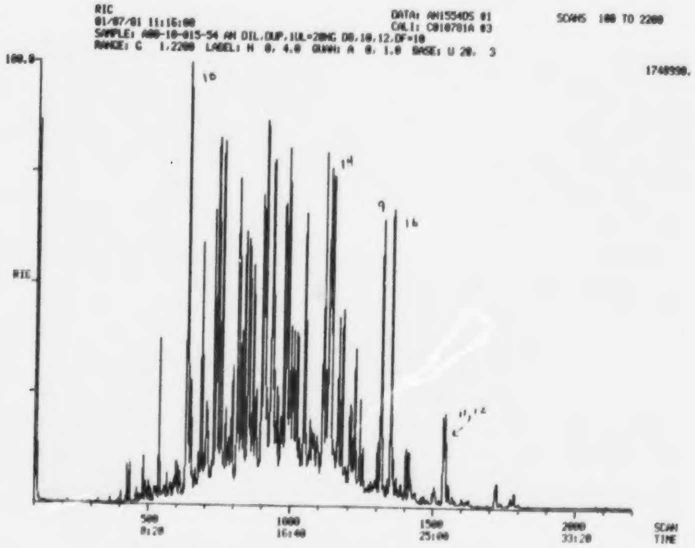


(b) Creosote oil/water separator -- bottom layer

Figure A-11. Chromatograms of creosote solutions through the process.



(c) Creosote working solution



(d) Creosote retort drips

Figure A-11. Concluded

TABLE A-7. SAMPLE NUMBER AND IDENTIFICATION

Sample No.	Sample Description
1	Pond, top layer w/oil, 1 of 2
2	Pond, top layer w/oil, 2 of 2
3	Pond, sludge
4	Pond, middle layer
5	Creosote pan evap. liquid, 1700, 9/23/80
6	Creosote oil/water separator, top layer, 9/23/80
7	Creosote oil/water separator, bottom layer, 9/28/80
8	Creosote retort drips, 1158, 9/23/80
9	Penta fugitive emission, front half
10	Penta fugitive emission, back half
11	Penta retort drips, 1138
12	Penta oil/water separator, top layer
13	Creosote pan evap. liquid and impinger H_2O, front half
14	Creosote pan evap. liquid and impinger 1 H_2O, front half, rinse
15	Creosote pan evap. liquid and impingers 2 and 3 H_2O, test 1, back half, rinse
16	Creosote oil/water separator, top layer
17	Creosote oil/water separator, bottom layer
18	Creosote pan evap. liquid, pretest
19	Creosote pan evap. liquid, test 2, front half
20	Creosote pan evap. liquid, test 2
21	Creosote pan evap. liquid, test 2 probe rinse
22	Penta pan evap. liquid, test 2 impinger H_2O
23	Penta pan evap. liquid, test 1, front half rinse
24	Penta pan evap. liquid, pretest 1
25	Penta pan evap. liquid, test 2
26	Penta pan evap. liquid, test 1, back half
27	Penta fugitive emission, test 2, front half
28	Penta pan evap. liquid, test 2, front half
29	Penta oil/water separator, top layer
30	Penta pan evap. liquid, test 1, back half rinse
31	Penta pan evap. liquid, test 1, front half, impinger H_2O
32	Penta oil/water separator, bottom layer
33	Penta pan evap. liquid, test 3, impinger H_2O
34	Penta pan evap. liquid, test 4, impinger H_2O
35	Penta pan evap., bottoms from value 6 in. off ground
36	Penta retort fugitive emission, test 3, impinger H_2O
37	Penta pan evap. liquid, test 3
38	Penta 40 percent solid in No. 2 fuel oil
39	Penta retort fugitive emission, test 3, front half, $MeCl_2$ rinse
40	Penta pan evap. liquid, test 3, fron half, $MeCl_2$ rinse

TABLE A-7. Concluded

Sample No.	Sample Description
41	Penta pan evap. liquid, test 4, front half, $MeCl_2$ rinse
42	Penta oil/water separator, bottom layer
43	Penta retort drips
44	Creosote pan evap. liquid, test 4, impinger H_2O
45	Creosote pan evap. liquid, test 3, impinger H_2O
46	Creosote pan evap. liquid, test 3, front half
47	Creosote pan evap. liquid, test 4
48	Creosote retort fugitive emission, test 1, front half, impinger H_2O
49	Creosote oil/water separator, bottom layer
50	Creosote retort fugitive emmisson test 1, front half, $MeCL_2$ rinse
51	Penta oil/water separator, top layer and oil
52	Creosote pan evap. liquid, test 3
53	Creosote pan evap. bottoms
54	Creosote retort drips
55	Creosote pan evap. liquid, test 4, front half, $MeCL_2$ rinse
56	Creosote oil/water separator, top layer
57	Creosote working solution, tank 5 (new)
58	Penta working solution, as used
59	Penta pan evap. liquid, test 4
60	$MeCl_2$ blank, baker res. anal.
61	Viking DIH_2O, all tests after 9/24
62	Well No. 4
63	XAD, penta pan evap. liquid, test 1
64	XAD blank No. 2
65	XAD, penta pan evap. liquid, test 4
66	
67	
68	XAD, creosote pan evap. liquid, test 4
69	XAD, creosote pan evap. liquid, test 3
70	XAD, creosote pan evap. liquid, test 1
71	XAD, penta fugitive emission, test 1
72	XAD, creosote pan evap. liquid, test 2
73	XAD, penta fugitive emission, test 2
74	XAD, creosote pan evap. liquid, test 3
75	XAD, penta fugitive emission, test 3
76	

type & cut in

TABLE A-8. WOOD PRESERVING TEST RESULTS

TEST CPEOSOTE PAN EVAP TEST 1

TEST DATE 9/23/80

	Liquid	OW Sep Top	OW Sep Bot	XAD
COMPOUND Acurex I.D. # 80-10-015-	-5	-6	-7	-70
Pentachlorophenol	2.3	0.5	360	0.45
Phenol	<0.5	15	<100	0.08
Fluoranthene	7.8	7.0	3500	0.67
Naphthalene	33	30	18000	2.0
Benzo(a)anthracene	15	11	9800	0.009
Benzo(a)pyrene	7.5	3.9	2400	<0.01
Benzofluoranthenes	13	10	2200	<0.01
Chrysene	12	7.6	5300	0.007
Acenaphthylene	76	36	2200	0.061
Anthracene	12	8.2	300	0.33
Benzo(ghi)perylene	3.2	1.4	<100	<0.01
Fluorene	50	25	11000	0.059
Phenanthrene	35	20	2500	2.00
Dibenzo(a,h)anthracene	0.7	<1	120	<0.01
Indeno(1,2,3-cd)pyrene	3.0	<1	<100	<0.01
Pyrene	6.5	5.8	680	0.48
Benzene	<0.1	0.1	26	NA
Toluene	0.1	0.1	140	NA
Ethylbenzene	0.5	<0.1	44	NA

All concentrations in units of micrograms per gram except for XAD collections which are total milligrams collected.

TABLE A-9. WOOD PRESERVING TEST RESULTS

WOOD PRESERVING TEST RESULTS

TEST SITE: MINNESOTA

TEST CREOSOTE TEST 1

TEST DATE 9/23/80

	Retort Drips			
COMPOUND Acurex I.D. # 80-10-015-	-8			
Pentachlorophenol	390			
Phenol	<20			
Fluoranthene	420			
Naphthalene	1300			
Benzo(a)anthracene	870			
Benzo(a)pyrene	240			
Benzofluoranthenes	700			
Chrysene	710			
Acenaphthylene	72			
Anthracene	1200			
Benzo(ghi)perylene	<50			
Fluorene	1100			
Phenanthrene	2300			
Dibenzo(a,h)anthracene	<50			
Indeno(1,2,3-cd)pyrene	<50			
Pyrene	370			
Benzene	0.3			
Toluene	<0.2			
Ethylbenzene	<0.2			

NOTE: Fugitives washes from 9/25/80 were added to this XAD sample by mistake.

All concentrations in units of micrograms per gram except for XAD collections which are total milligrams collected.

TABLE A-10. WOOD PRESERVING TEST RESULTS

TEST CREOSOTE PAN EVAP TEST 2

TEST DATE 9/24/80

COMPOUND Acurex I.D. # 80-10-015-	Pre Test Liquid 8:30 -18	O.W. Sep Top -16	O.W. SepBot -17	XAD -72
Pentachlorophenol	3.4	12	3600	<0.1
Phenol	11	7	1500	23
Fluoranthene	20	20	33000	38
Naphthalene	13	42	33000	310
Benzo(a)anthracene	14	10	23000	0.6
Benzo(a)pyrene	24	2	610	<0.05
Benzofluoranthenes	5.7	4	530	0.08
Chrysene	8.9	10	19000	0.5
Acenaphthylene	1.2	2	3400	11
Anthracene	9.9	7	69000	49
Benzo(ghi)perylene	0.6	0.2	<500	<0.1
Fluorene	2.5	16	38000	170
Phenanthrene	3.2	19	41000	150
Dibenzo(a,h)anthracene	0.9	0.2	<500	<0.1
Indeno(1,2,3-cd)pyrene	0.7	0.3	<500	<0.1
Pyrene	16	15	27000	24
Benzene	<0.1	<0.1	<50	NA
Toluene	<0.1	<0.1	<50	NA
Ethylbenzene	<0.1	<0.1	<50	NA

All concentrations in units of micrograms per gram except for XAD collections which are total milligrams collected.

TABLE A-11. WOOD PRESERVING TEST RESULTS

TEST CREOSOTE PAN EVAP TEST 2

TEST DATE 9/24/80

	Liquid #2			
COMPOUND Acurex I.D. # 80-10-015-	-20			
Pentachlorophenol	13			
Phenol	14			
Fluoranthene	64			
Naphthalene	18			
Benzo(a)anthracene	41			
Benzo(a)pyrene	1.7			
Benzofluoranthenes	2.1			
Chrysene	26			
Acenaphthylene	3.7			
Anthracene	26			
Benzo(ghi)perylene	< 0.4			
Fluorene	75			
Phenanthrene	91			
Dibenzo(a,h)anthracene	0.4			
Indeno(1,2,3-cd)pyrene	< 0.4			
Pyrene	48			
Benzene	< 0.1			
Toluene	< 0.1			
Ethylbenzene	< 0.1			

All concentrations in units of micrograms per gram except for XAD collections which are total milligrams collected.

TABLE A-12. WOOD PRESERVING TEST RESULTS

TEST CREOSOTE PAN EVAP

TEST DATE 9/25/80 TEST 3

	Liquid	Pan Bottoms	Working Soln.	XAD
COMPOUND Acurex I.D. # 80-10-015-	-52	-53	-57	-74
Pentachlorophenol	7.6	260	1700	2.8
Phenol	31	30	400	60
Fluoranthene	9.3	590	32000	20
Naphthalene	10	680	24000	2800
Benzo(a)anthracene	4.5	390	20000	1.4
Benzo(a)pyrene	0.6	91	600	0.25
Benzofluoranthenes	1.4	190	650	0.69
Chrysene	3.7	240	15000	1.2
Acenaphthylene	0.3	840	5700	30
Anthracene	2.8	260	12000	70
Benzo(ghi)perylene	<0.1	10	<500	<0.1
Fluorene	8.9	660	36000	560
Phenanthrene	15	1100	37000	200
Dibenzo(a,h)anthracene	<0.1	<10	<500	<0.1
Indeno(1,2,3-cd)pyrene	0.1	16	<500	<0.1
Pyrene	6.7	440	27000	13
Benzene	<0.1	6.7	26	NA
Toluene	<0.1	1.4	2.7	NA
Ethylbenzene	<0.1	0.3	<0.5	NA

All concentrations in units of micrograms per gram except for XAD collections which are total milligrams collected.

TABLE A-16

TABLE A-13. WOOD PRESERVING TEST RESULTS

WOOD PRESERVING TEST RESULTS

TEST SITE: MINNESOTA

TEST CREOSOTE TEST 3

TEST DATE

	Retort Drips			
COMPOUND Acurex I.D. # 80-10-015-	-54			
Pentachlorophenol	1800			
Phenol	<10			
Fluoranthene	200			
Naphthalene	1400			
Benzo(a)anthracene	1000			
Benzo(a)pyrene	200			
Benzofluoranthenes	500			
Chrysene	850			
Acenaphthylene	180			
Anthracene	1500			
Benzo(ghi)perylene	40			
Fluorene	2600			
Phenanthrene	2200			
Dibenzo(a,h)anthracene	20			
Indeno(1,2,3-cd)pyrene	52			
Pyrene	1700			
Benzene	15			
Toluene	< 1			
Ethylbenzene	< 1			

All concentrations in units of micrograms per gram except for XAD collections which are total milligrams collected.

TABLE A-14. WOOD PRESERVING TEST RESULTS

TEST CREOSOTE PAN EVAP TEST 4

TEST DATE 9/25/80

COMPOUND Acurex I.D. # 80-10-015-	Liquid -47	OW Sep Top -56	OW Sep Bot -49	XAD -68
Pentachlorophenol	0.5	8.3	1300	2.0
Phenol	35	5.2	800	<0.4
Fluoranthene	6.0	140	13000	27
Naphthalene	6.4	200	38000	2800
Benzo(a)anthracene	2.4	60	9200	1.5
Benzo(a)pyrene	0.4	6.1	3000	0.40
Benzofluoranthenes	0.8	15	500	1.7
Chrysene	1.9	50	5400	1.1
Acenaphthylene	0.2	6	5700	56
Anthracene	1.4	56	8000	56
Benzo(ghi)perylene	<0.1	<10	730	<0.4
Fluorene	6.0	110	35000	740
Phenanthrene	12	190	22000	330
Dibenzo(a,h)anthracene	<0.1	<10	1500	<0.4
Indeno(1,2,3-cd)pyrene	<0.1	<10	1300	<0.4
Pyrene	4.2	100	10000	20
Benzene	3.4	<0.1	27	NA
Toluene	<0.2	<0.1	0.5	NA
Ethylbenzene	0.3	<0.1	6.8	NA

All concentrations in units of micrograms per gram except for XAD collections which are total milligrams collected.

TABLE A-15. WOOD PRESERVING TEST RESULTS

TEST PCP PAN EVAP TEST 1

TEST DATE 9/23/80

	Retort Drips	OW Sep Top		XAD
COMPOUND Acurex I.D. # 80-10-015-	-11	-12		-71
Pentachlorophenol	1500	25000		<0.01
Phenol	< 10	<10		<0.01
Fluoranthene	29	21		0.012
Naphthalene	50	1800		0.026
Benzo(a)anthracene	60	<10		<0.01
Benzo(a)pyrene	50	20		<0.01
Benzofluoranthenes	54	20		<0.01
Chrysene	50	60		<0.01
Acenaphthylene	16	200		0.062
Anthracene	47	240		0.012
Benzo(ghi)perylene	< 10	<10		<0.01
Fluorene	110	1500		<0.01
Phenanthrene	150	3000		0.14
Dibenzo(a,h)anthracene	< 10	< 10		<0.01
Indeno(1,2,3-cd)pyrene	< 10	< 10		<0.01
Pyrene	24	< 10		<0.01
Benzene	< 0.5	<0.5		NA
Toluene	< 0.5	65		NA
Ethylbenzene	< 0.5	41		NA

All concentrations in units of micrograms per gram except for XAD collections which are total milligrams collected.

TABLE A-16. WOOD PRESERVING TEST RESULTS

TEST PCP PAN EVAP TEST 2

TEST DATE 9/24/80

	Liquid 17:15	OW Sep Top	OW Sep Bot	XAD
COMPOUND Acurex I.D. # 80-10-015-	-25	-29	-32	-63
Pentachlorophenol	70	14000	40000	32
Phenol	1.2	<10	<10	<0.01
Fluoranthene	5.2	970	3800	1.80
Naphthalene	0.1	1500	3700	3.5
Benzo(a)anthracene	1.6	200	540	0.20
Benzo(a)pyrene	0.1	40	110	<0.05
Benzofluoranthenes	<0.1	110	380	<0.05
Chrysene	1.2	180	520	0.18
Acenaphthylene	0.1	310	140	<0.05
Anthracene	0.4	180	400	0.30
Benzo(ghi)perylene	<0.1	<10	30	<0.05
Fluorene	0.3	850	2700	<0.05
Phenanthrene	2.6	1800	5000	1.8
Dibenzo(a,h)anthracene	<0.1	<10	4	<0.05
Indeno(1,2,3-cd)pyrene	<0.1	<10	15	<0.05
Pyrene	3.6	710	3500	1.50
Benzene	<0.2	<10	0.3	NA
Toluene	0.3	<10	27	NA
Ethylbenzene	<0.2	<10	19	NA

All concentrations in units of micrograms per gram except for XAD collections which are total milligrams collected.

TABLE A-17. WOOD PRESERVING TEST RESULTS

TEST PCP PAN TEST 2

TEST DATE 9/24/80

COMPOUND Acurex I.D. # 80-10-015-	Liquid 9:00 -24	Fugitive XAD -73		
Pentachlorophenol	140	5.0		
Phenol	0.5	1.3		
Fluoranthene	7.9	<0.1		
Naphthalene	0.4	3.6		
Benzo(a)anthracene	3.7	<0.1		
Benzo(a)pyrene	0.1	<0.1		
Benzofluoranthenes	0.1	<0.1		
Chrysene	3.7	<0.1		
Acenaphthylene	0.1	0.18		
Anthracene	1.2	0.03		
Benzo(ghi)perylene	< 0.1	<0.5		
Fluorene	1.4	0.2		
Phenanthrene	9.5	0.3		
Dibenzo(a,h)anthracene	<0.1	<0.5		
Indeno(1,2,3-cd)pyrene	<0.1	<0.5		
Pyrene	6.1	<0.1		
Benzene	<0.1	NA		
Toluene	<0.1	NA		
Ethylbenzene	<0.1	NA		

All concentrations in units of micrograms per gram except for XAD collections which are total milligrams collected.

TABLE A-18. WOOD PRESERVING TEST RESULTS

WOOD PRESERVING TEST RESULTS

TEST SITE: MINNESOTA

TEST PCP PAN EVAP TEST 3

TEST DATE 9/25/80

	LIQUID	O.W.SEP TOP	O.W. SEP BOT	PAN BOTTOMS
COMPOUND Acurex I.D. # 80-10-015-	-37	-51	-42	-35
Pentachlorophenol	70	45,000	980	62
Phenol	0.4	<10	<10	1.2
Fluoranthene	2.7	2,800	2,000	2.0
Naphthalene	0.1	2,000	220	1.1
Benzo(a)anthracene	1.4	430	290	0.5
Benzo(a)pyrene	< 0.1	96	68	0.05
Benzofluoranthenes	< 0.1	320	190	0.2
Chrysene	1.0	400	420	0.4
Acenaphthylene	0.3	370	1600	0.05
Anthracene	0.4	1100	400	0.5
Benzo(ghi)perylene	< 0.1	7	< 20	<0.1
Fluorene	2.6	2400	2100	1.0
Phenanthrene	2.4	4000	3600	3.5
Dibenzo(a,h)anthracene	< 0.1	<10	<20	< 0.1
Indeno(1,2,3-cd)pyrene	< 0.1	28	<20	< 0.1
Pyrene	2.0	1900	1300	1.4
Benzene	< 0.2	1.2	0.2	<0.2
Toluene	< 0.2	77	0.1	0.3
Ethylbenzene	< 0.2	2.3	1.2	<0.2

All concentrations in units of micrograms per gram except for XAD collections which are total milligrams collected.

TABLE A-19. WOOD PRESERVING TEST RESULTS

TEST PCP PAN EVAP TEST 3

TEST DATE 9/25/80

COMPOUND Acurex I.D. # 80-10-015-	XAD -69	Fugitive XAD -75	40% PCP in oil -38	Retort Drips -43
Pentachlorophenol	45	1.7	490,000	2100
Phenol	0.85	< 0.01	<1,000	<10
Fluoranthene	6.8	0.012	<1,000	180
Naphthalene	3.9	1.2	<1,000	200
Benzo(a)anthracene	0.38	<0.01	<1,000	80
Benzo(a)pyrene	< 0.3	<0.01	<1,000	5.6
Benzofluoranthenes	< 0.3	<0.01	<1,000	26
Chrysene	0.34	<0.01	<1,000	85
Acenaphthylene	1.7	0.074	<1,000	11
Anthracene	3.0	0.019	<1,000	55
Benzo(ghi)perylene	< 0.5	<0.01	<5,000	<5
Fluorene	4.0	0.30	<1,000	140
Phenanthrene	12	0.18	<1,000	320
Dibenzo(a,h)anthracene	<0.5	<0.10	<5,000	<5
Indeno(1,2,3-cd)pyrene	<0.5	<0.10	<5,000	<5
Pyrene	4.2	0.01	<1,000	140
Benzene	NA	NA	<10	0.1
Toluene	NA	NA	12	0.5
Ethylbenzene	NA	NA	31	0.5

All concentrations in units of micrograms per gram except for XAD collections which are total milligrams collected.

TABLE A-20. WOOD PRESERVING TEST RESULTS

TEST PCP PAN EVAP TEST 4

TEST DATE 9/25/80

COMPOUND Acurex I.D. # 80-10-015-	PCP Working Soln. -58	Liquid -59	XAD -65	
Pentachlorophenol	44000	41	24000	
Phenol	< 200	0.3	420	
Fluoranthene	430	1.2	1400	
Naphthalene	3800	0.3	4700	
Benzo(a)anthracene	<100	0.9	160	
Benzo(a)pyrene	<100	<0.1	<10	
Benzofluoranthenes	<100	<0.1	35	
Chrysene	<100	0.7	150	
Acenaphthylene	170	0.1	300	
Anthracene	230	0.2	600	
Benzo(ghi)perylene	<200	<0.1	<10	
Fluorene	1100	1.7	1400	
Phenanthrene	1700	1.5	1200	
Dibenzo(a,h)anthracene	<200	<0.1	<10	
Indeno(1,2,3-cd)pyrene	<200	<0.1	<10	
Pyrene	350	0.9	1100	
Benzene	<1	<0.2	NA	
Toluene	18	0.2	NA	
Ethylbenzene	23	0.2	NA	

All concentrations in units of micrograms per gram except for XAD collections which are total milligrams collected.

TABLE A-21. WOOD PRESERVING TEST RESULTS

WOOD PRESERVING TEST RESULTS

TEST SITE: ______ **TEST** Plant D

TEST DATE 11/19/80

COMPOUND Field Acurex I.D. # A80-11-043	116-93	121-104	117-94	120-103
Description	Sludge	Sludge	Aeration Tank	Aeration Tank
Pentachlorophenol	550	NA	2.4	NA
Phenol	<1.0		0.2	
Fluoranthene	3.3		<0.01	
Naphthalene	17		0.05	
Benzo(a)anthracene	<1.0		<0.01	
Benzo(a)pyrene	<1.0		<0.01	
Benzofluoranthenes	<1.0		<0.01	
Chrysene	<1.0		<0.01	
Acenaphthylene	<1.0		0.01	
Anthracene	<1.0		0.01	
Benzo(ghi)perylene	<1.0		<0.01	
Fluorene	9.3		0.03	
Phenanthrene	35		0.04	
Dibenzo(a,h)anthracene	<1.0		<0.01	
Indeno(1,2,3-cd)pyrene	<1.0		<0.01	
Pyrene	1.7	↓	<0.01	↓
Benzene	NA	<0.02	NA	<0.005
Toluene	NA	<0.02	NA	<0.005
Ethylbenzene	NA	<0.02	NA	<0.005

All concentrations in units of micrograms per gram except for XAD collections which are total milligrams collected.

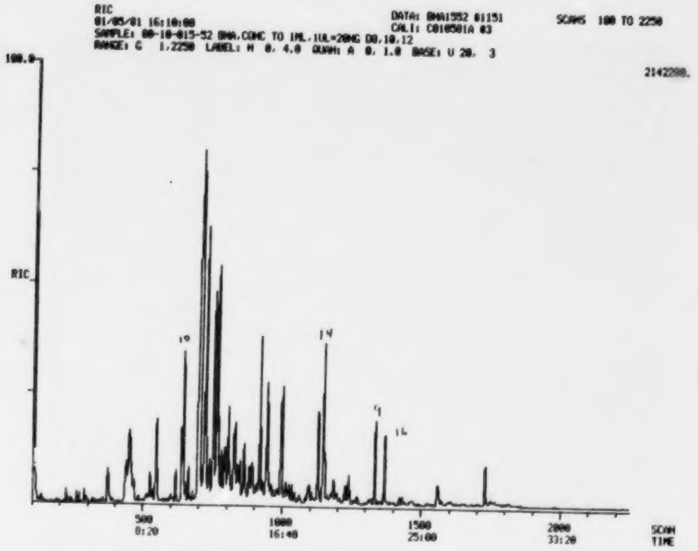
TABLE A-21. Concluded

WOOD PRESERVING TEST RESULTS **TEST** Plant D

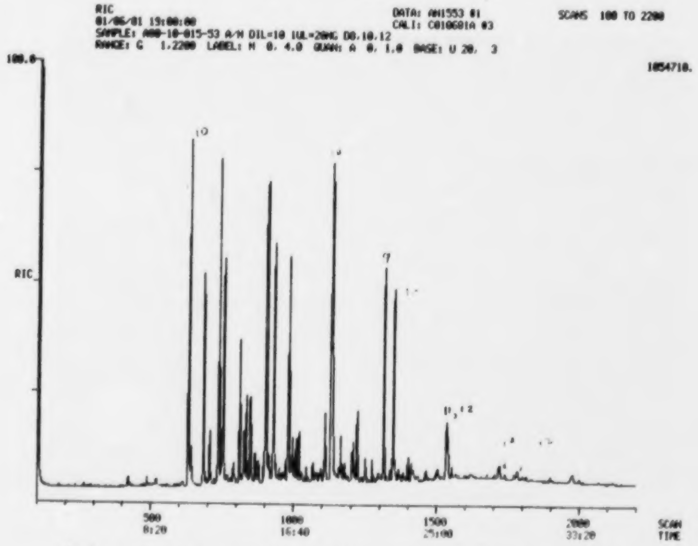
TEST SITE: **TEST DATE** 11/19/80

Field I.D.	118	119		
COMPOUND Acurex I.D. # A80-11-043	-95	-102		
Description	Condenser	Condenser		
Pentachlorophenol	32	NA		
Phenol	2.4	↓		
Fluoranthene	1.8			
Naphthalene	3.2			
Benzo(a)anthracene	0.3			
Benzo(a)pyrene	<0.1			
Benzofluoranthenes	<0.1			
Chrysene	0.3			
Acenaphthylene	0.2			
Anthracene	0.6			
Benzo(ghi)perylene	<0.1			
Fluorene	1.8			
Phenanthrene	3.7			
Dibenzo(a,h)anthracene	<0.1			
Indeno(1,2,3-cd)pyrene	<0.1			
Pyrene	1.1			
Benzene	NA	0.02		
Toluene	NA	0.13		
Ethylbenzene	NA	0.04		

All concentrations in units of micrograms per gram except for XAD collections which are total milligrams collected.

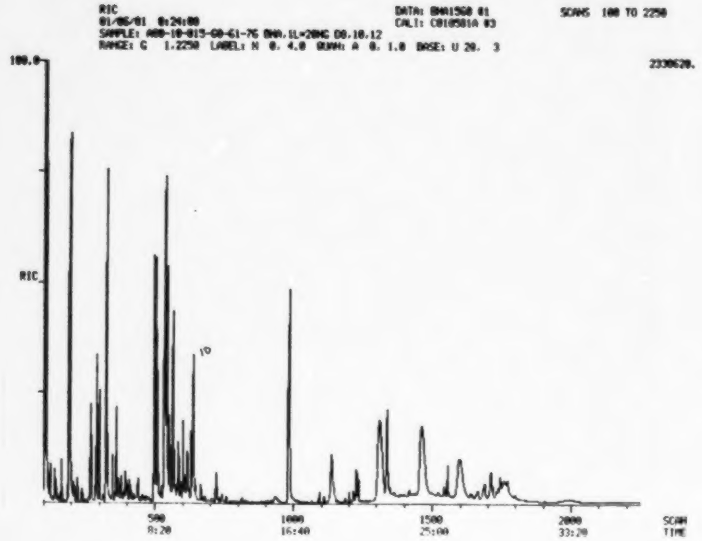


(a) Creosote charge liquid to pan evaporator

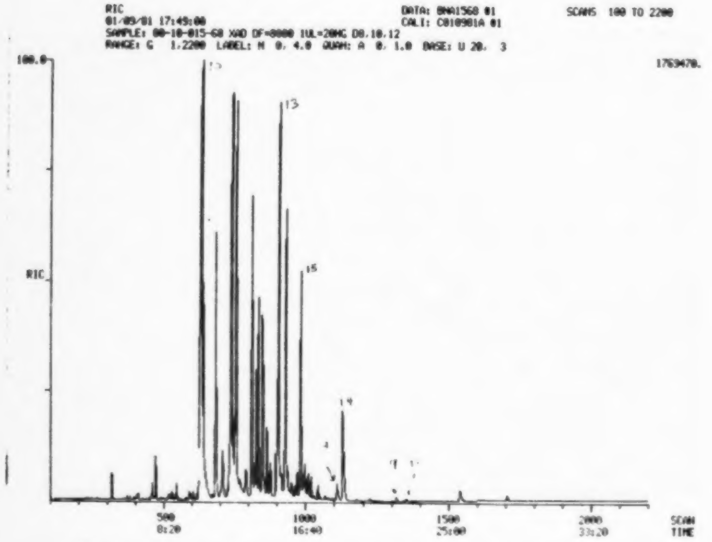


(b) Creosote partially evaporated liquid

Figure A-12. Chromatograms from creosote wastewater pan evaporation process.

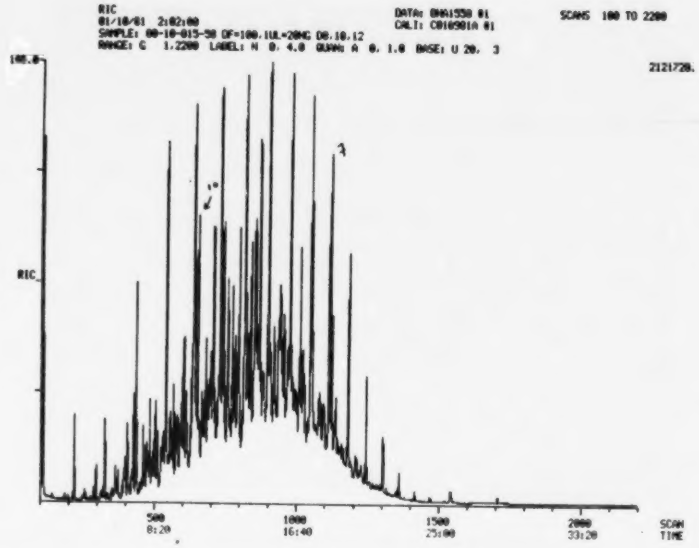


(c) XAD-2 blank

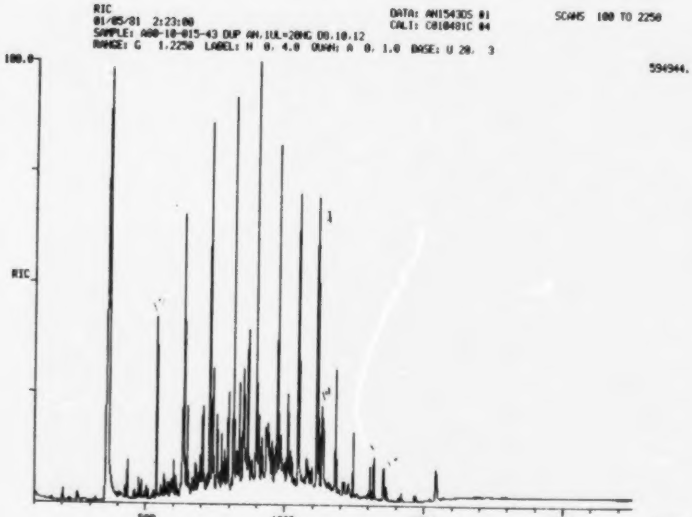


(d) Creosote pan evaporator XAD-2

Figure A-12. Concluded

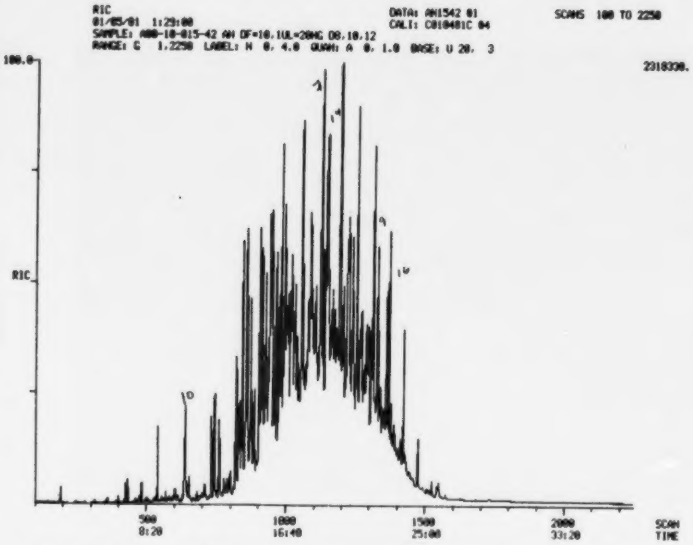


(a) Penta working solution

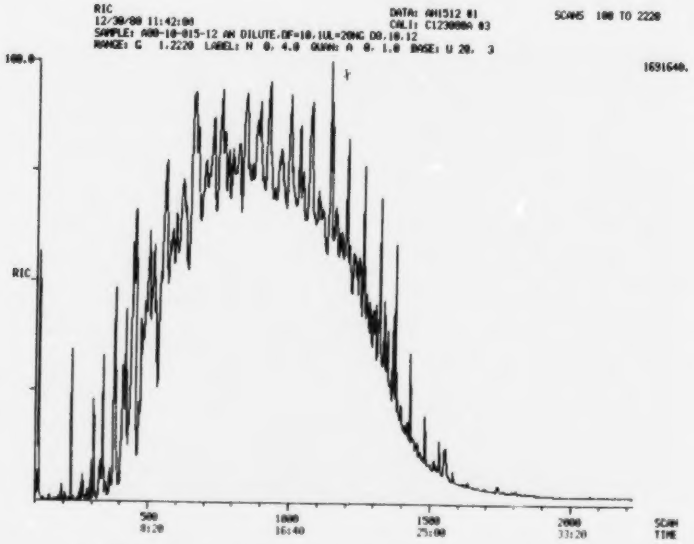


(b) Penta retort drips

Figure A-13. Chromatograms of penta process samples.

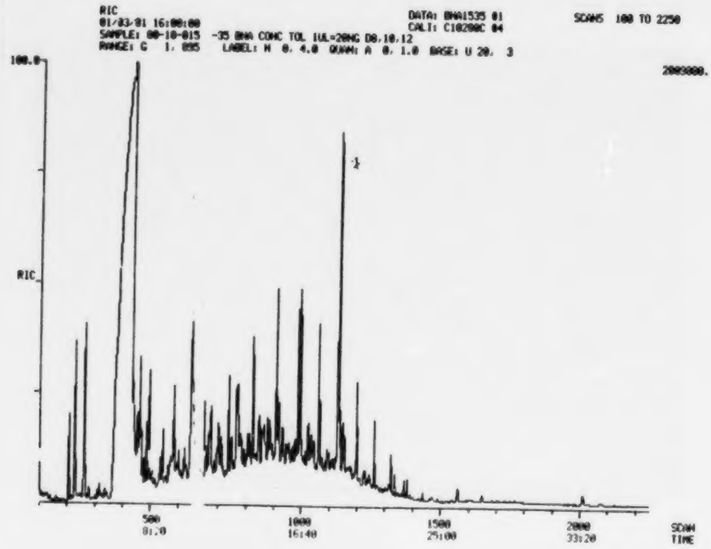


(c) Penta oil/water separator -- bottom layer

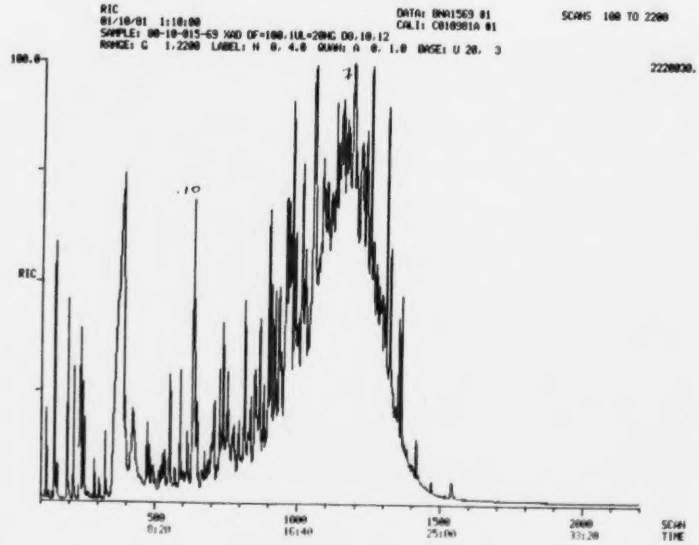


(d) Penta oil/water separator -- top layer

Figure A-13. Concluded

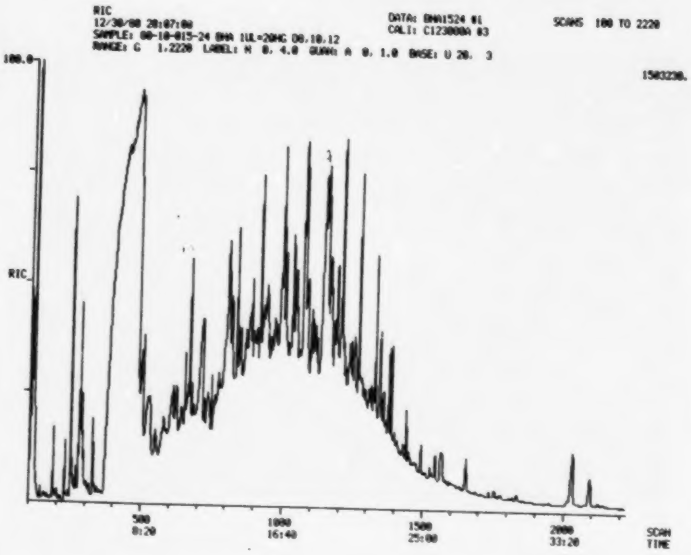


(a) Penta pan bottoms



(b) Penta XAD-2

Figure A-14. Chromatograms of samples from penta evaporation process.



(c) Penta test liquid

Figure A-14. Concluded

APPENDIX B

CHARACTERIZATION OF MULTIMEDIA EMISSIONS FROM SPRAY EVAPORATION OF WOOD PRESERVING WASTEWATERS

Raw data for sample identification and field data on this study has been compiled and is available upon request. Copies may be obtained from EPA IERL-Ci 26 W. St. Clair Street, Cincinnati, OH 45268 (513/684-4227).

This field test program was carried out at plant B and is described in Section 6.

B.1 TEST SITE

Table B-1 presents a summary of the treated wood production for the field test period. Figure B-1 presents a photograph of the pond in operation.

B.2 FIELD TEST PROGRAM

The following subsections describe the methods and procedures employed during sampling.

TABLE B-1. TREATED WOOD PRODUCTION DURING SAMPLING PERIOD

	Period 11-18-80 to 11-20-80			
	Creosote		Penta	
	m^3	ft^3	m^3	ft^3
11-18	39.7	1,403	77.0	2,721
11-19	85.3	3,013	77.8	2,749
11-20	40.5	1,432	86.1	3,039
Total	165.5	5,848	240.9	8,509

Southern yellow pine -- utility poles

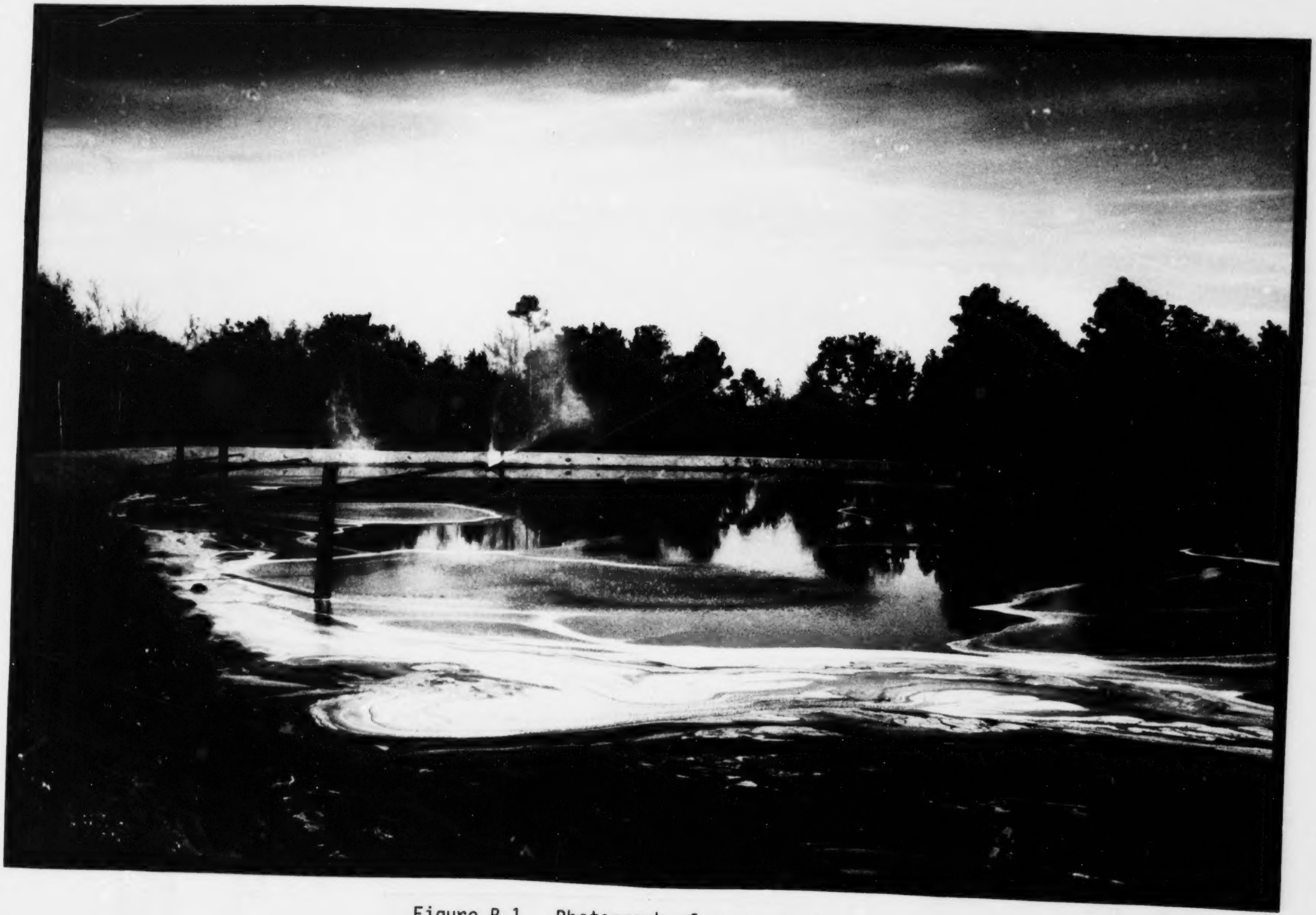


Figure B-1. Photograph of spray pond.

B.2.1 Fugitive Emission Sampling at the Spray Pond

Sampling of fugitive emissions from the spray pond was conducted using the concentration profile apparatus (CPA) developed by the University of Arkansas, College of Engineering, Fayetteville, Arkansas. The CPA as used during the field test program consists of three devices and some auxiliary support equipment as follows.

Wind velocity profile and direction indicator

This device consists of a mast with cup anemometers positioned at 20 cm, 40 cm, 80 cm, 160 cm, 240 cm and 320 cm and a wind direction vane mounted on top. Anemometer rotation speed and wind direction is transmitted to appropriate recorders operated by a 12-volt (lead/acid) battery. The unit was obtained from C. W. Thorntwaite Associates (Model 106). Figure B-2 presents a diagram of the device as assembled for field use.

Dry bulb temperature device

This device consisted of a small metal cup filled with modeling clay, centered in a short section of white PVC pipe to shield the clay from radiant energy. These units were mounted on the mast with the cup anemometers using the same spatial arrangement described for the wind velocity profile mast. The temperature of the clay was measured periodically using a hand-held Doric digital temperature indicator and a small RTD thermocouple. Figure B-2 also presents a diagram of the dry bulb temperature devices as they were used in the field.

Air sampling device

This assembly is not an off-the-shelf item but was designed and constructed by the University of Arkansas College of Engineering. The device consists of a 2m mast equipped with holders at six positions for small (300 ml) Dewar flasks and U-tube cryogenic traps. Tube extenders, upstream of the traps, allow precise sample heights to be chosen and maintained. The downstream side of U-tube traps are connected to Matheson No. 602 air rotometers. Flow was maintained by a portable hand-evacuated vacuum tank which was modified during the course of testing to operate from a Thomas Teflon diaphragm vacuum pump. Figure B-3 presents a diagram of the construction details for this device. Figure B-4 presents a detailed construction view of the Dewar flask bracket assembly. Figure B-5 presents a photograph of the CPA in sampling position.

Sampling fugitive emissions from the spray ponds was performed using the CPA in conjunction with three different sample collection methods. These included cryogenic U-tube traps, and Tenax and XAD-2 microreticular adsorbents. In all cases the sampled gas/aerosol was routed through a specially modified midget impinger prior to entry into the appropriate sample trap. The midget impingers modified the Smith-Greenburg design by shortening the impinger stem which raised the impaction plate above the liquid collection area. The purpose of this modification was to separate and collect the

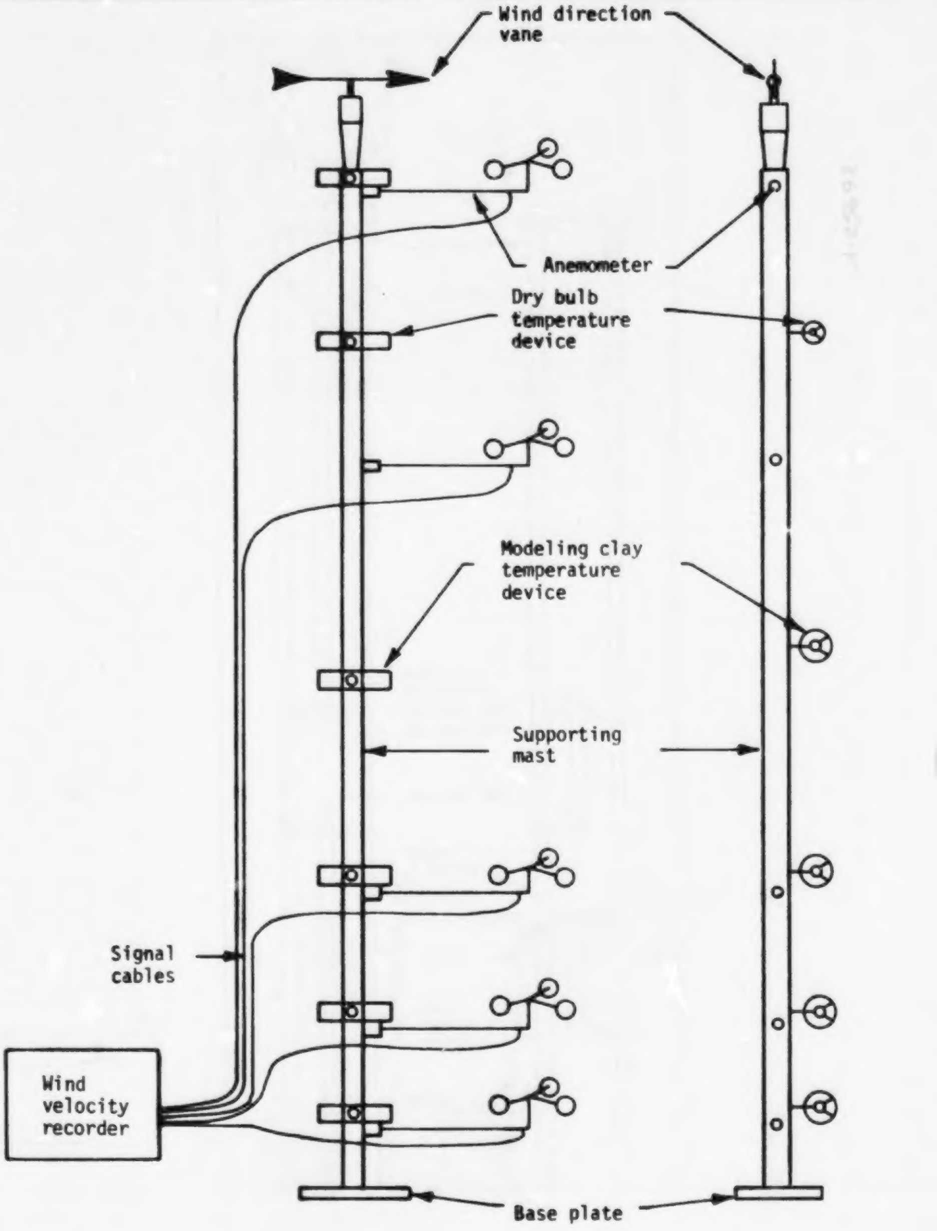

Wind direction vane
Anemometer
Dry bulb temperature device
Modeling clay temperature device
Supporting mast
Signal cables
Wind velocity recorder
Base plate

Figure B-2. Diagram of wind velocity profile and direction indicator and dry bulb temperature devices.

type

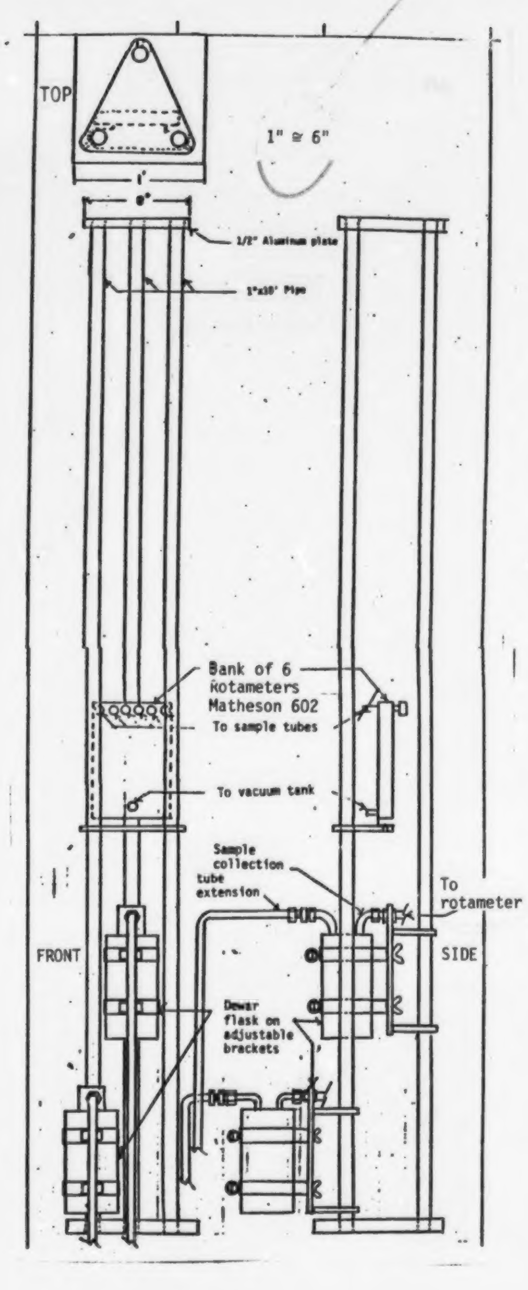

TOP
1" ≅ 6"
1'
8"
1/2" Aluminum plate
1"x10' Pipe
Bank of 6
Rotameters
Matheson 602
To sample tubes
To vacuum tank
Sample
collection
tube
extension
To
rotameter
FRONT
SIDE
Dewar
flask on
adjustable
brackets

Figure B-3. Construction details of air sampling device.

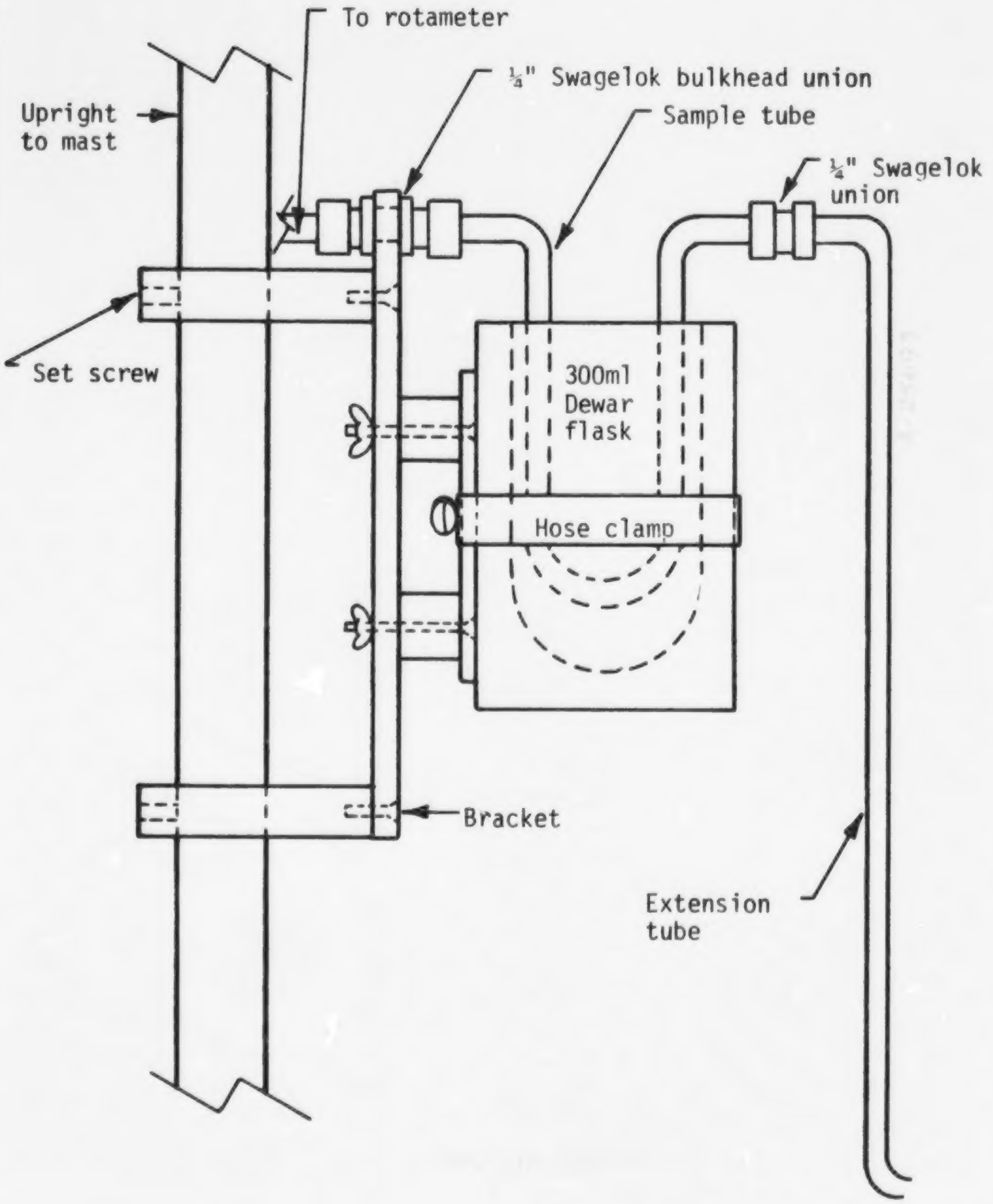

To rotameter
¼" Swagelok bulkhead union
Sample tube
Upright to mast
¼" Swagelok union
Set screw
300ml Dewar flask
Hose clamp
Bracket
Extension tube

Figure B-4. Detailed construction view of the Dewar flask bracket assembly.

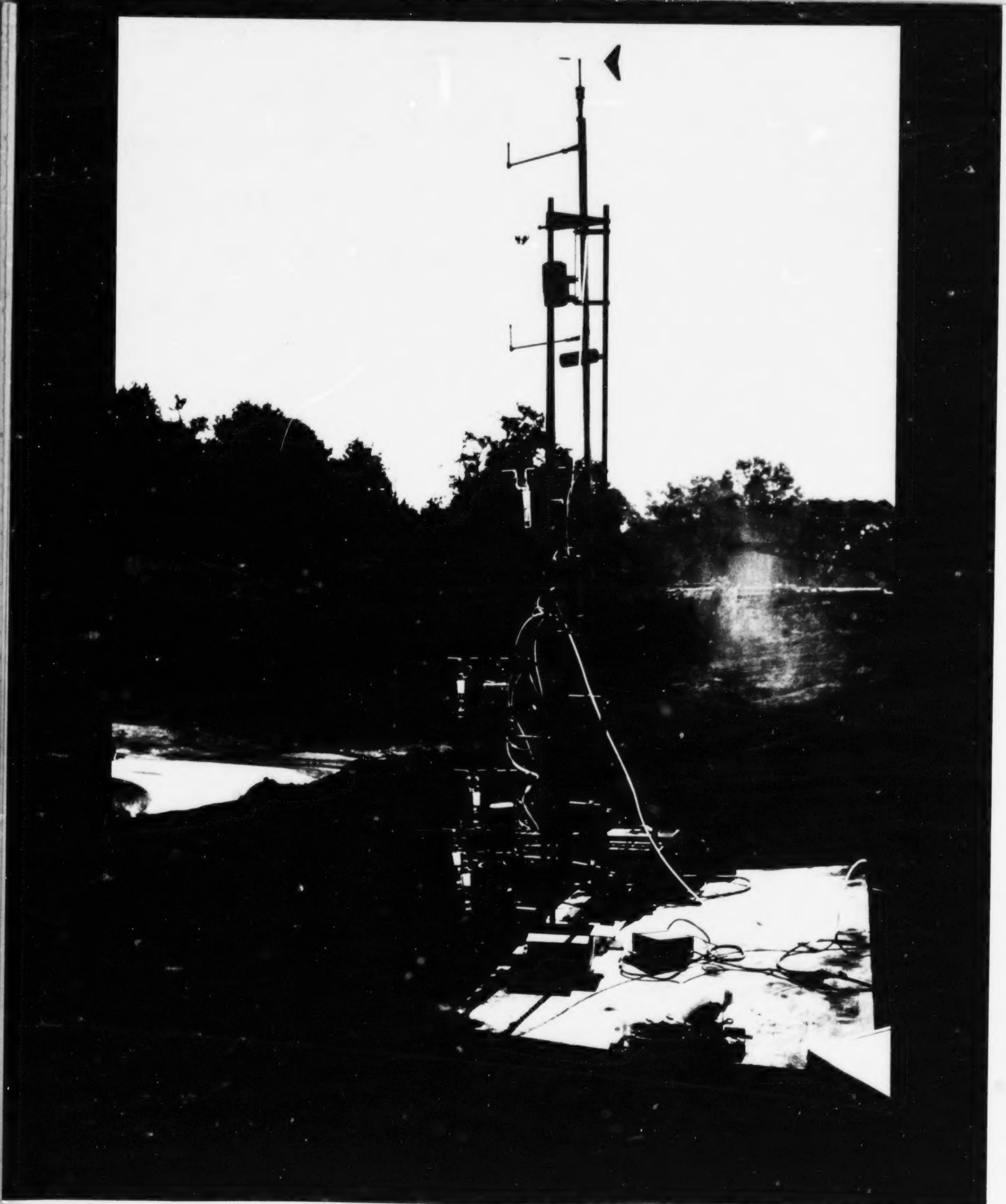


Figure B-5. Photograph of CPA in sampling position.

aerosol fraction of the sampled stream, ultimately extending the effective sampling time of the cryogenic U-tube traps by limiting the amount of freezable material entering the trap. Figure B-6 presents a diagram of the modified Smith-Greenburg midget impinger. The modified impingers were used in conjunction with all three sampling methods for the purpose of uniformity.

Cryogenic U-tube traps were constructed from 316 stainless steel tubing, 1/4-inch O.D. 0.020-inch wall thickness. Each tube was packed with glass beads ranging in size from 1.00 to 1.05 mm, purchased from B. Braun Melsungen, AKTIENGESELLSCHAFT, W. Germany. A small pyrex glass wool plug was inserted into each end of the packed U-tubes to retain the beads. Figure B-7 presents a diagram of the completed sampling device. Prior to use in the field the tubes were cleaned.

To effect sampling with the cryogenic U-tubes, the CPA was positioned at the optimum downwind location of the spray pond. The sample devices then were affixed to the CPA at the appropriate heights, with the body of the trap immersed in a liquid oxygen (LOX) bath. After sealing the sample inlet end of the U-tube, a leak test was performed by applying at least 10 inches of Mercury vacuum to the system and checking the rotometers for flow indication. If flow was noted, appropriate measures were taken to correct the leak.

After completion of a successful leak check, the specially modified midget impingers were connected and the actual sampling was begun. During the sampling period, the flow through each sample was maintained at 100 cc/min by adjusting the fine flow control valve mounted at the inlet of the rotometer. Figure B-8 presents a photograph of the cryogenic U-tube sampling device in sampling position (immersed in LOX bath).

The sample trial was terminated when two or more sample U-tubes became so restricted with frozen material and it was no longer possible to maintain the desired flow rate.

At the completion of sampling, the midget impinger and sample U-tubes were removed from the CPA and sealed. The U-tubes were placed on dry ice and maintained under dry ice conditions for their transport to the Mountain View, California laboratory. The modified Smith-Greenburg midget impingers were analytically rinsed with methylene chloride in the field laboratory. All rinses were collected and stored in precleaned 50 ml Wheaton glass sample vials with Teflon-lined septum caps. Rinses with methylene chloride prior to the next sample run were retained as blank solvent samples for that run.

The second type of trap for sampling in conjunction with the CPA utilized Tenax-GC microreticular adsorbent resin. The Tenax traps were constructed from 1/4-inch O.D. 2-mm bore ptrex tubing cut to 4-inch lengths. Prior to packing with Tenax, the tubes were muffled at 400°C for 4 hrs. The tubes were packed with Tenax GC, 80/100 mesh, using a small swatch of pyrex glass wool (also muffled) in each end to hold the adsorbent in place. The tubes were attached to the CPA with 316 stainless steel Swagelok nuts and Teflon ferrules to ensure a leakfree seal. Figure B-9 presents a diagram of the completed Tenax trap sampling device.

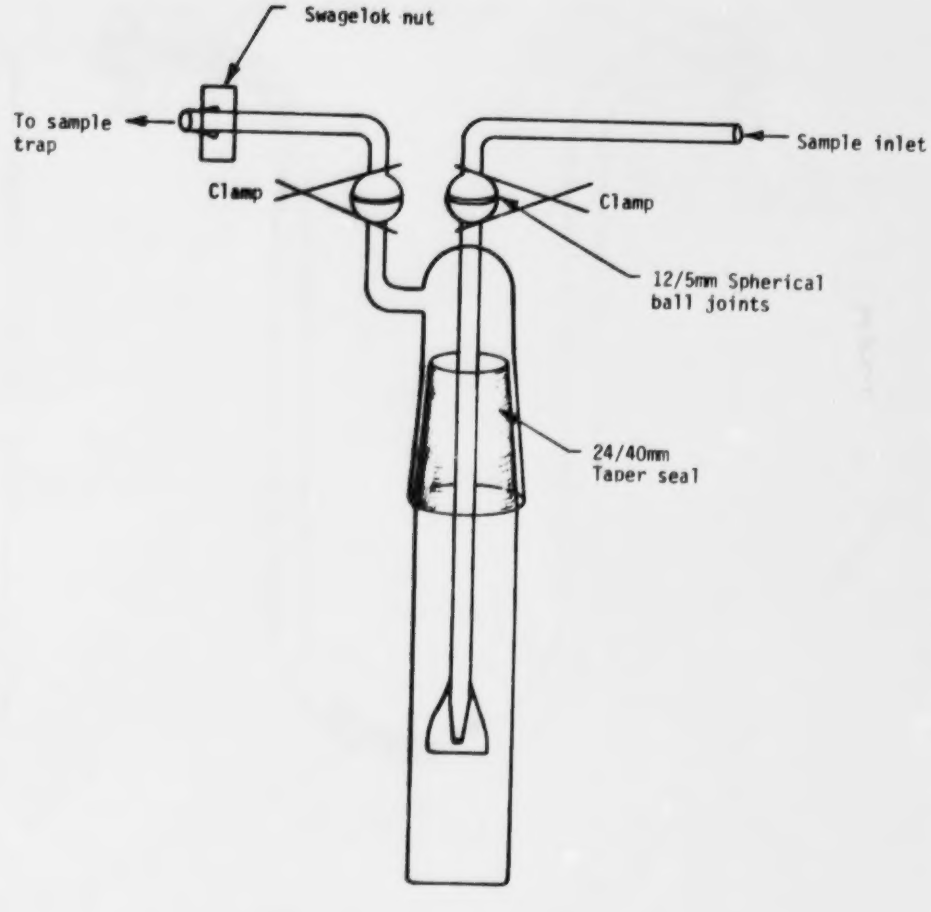

Swagelok nut
To sample trap
Sample inlet
Clamp
Clamp
12/5mm Spherical ball joints
24/40mm Taper seal

Figure B-6. Diagram of modified Smith-Greenburg midget impinger.

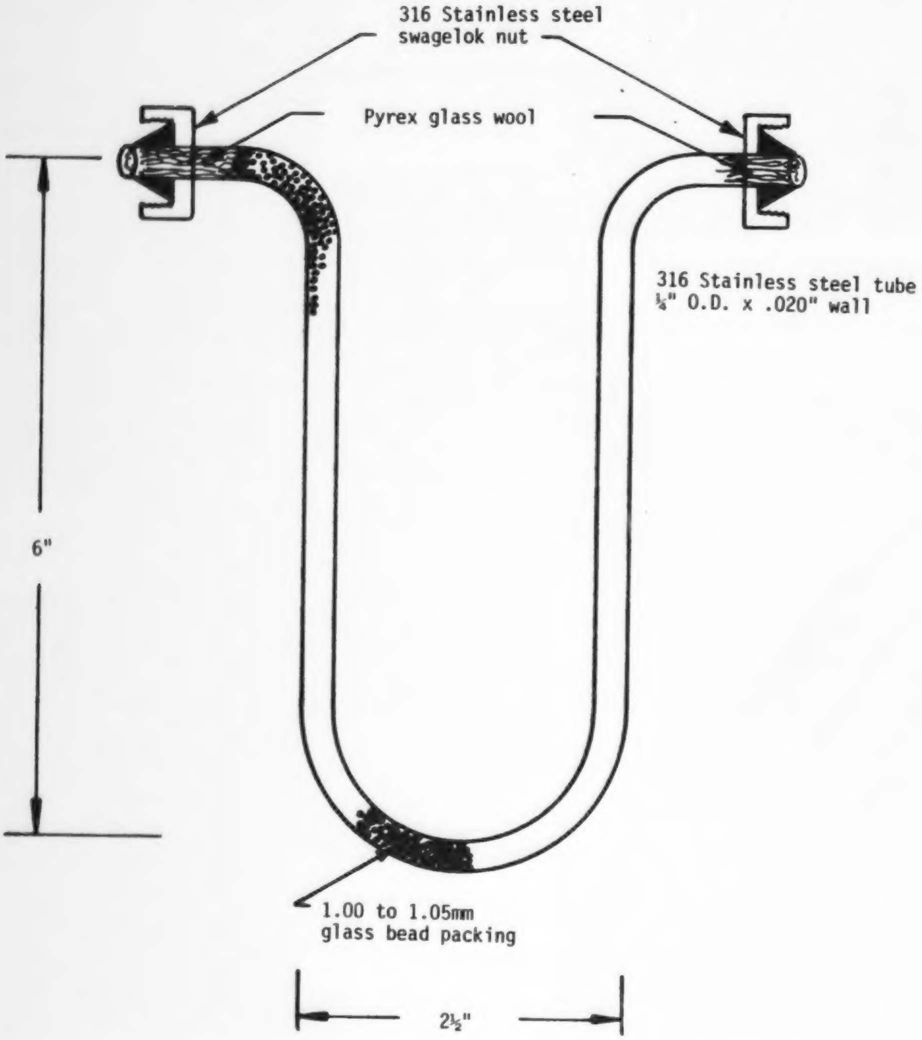

316 Stainless steel
swagelok nut
Pyrex glass wool
316 Stainless steel tube
¼" O.D. x .020" wall
6"
1.00 to 1.05mm
glass bead packing
2½"

Figure B-7. Cryogenic U-tube construction.

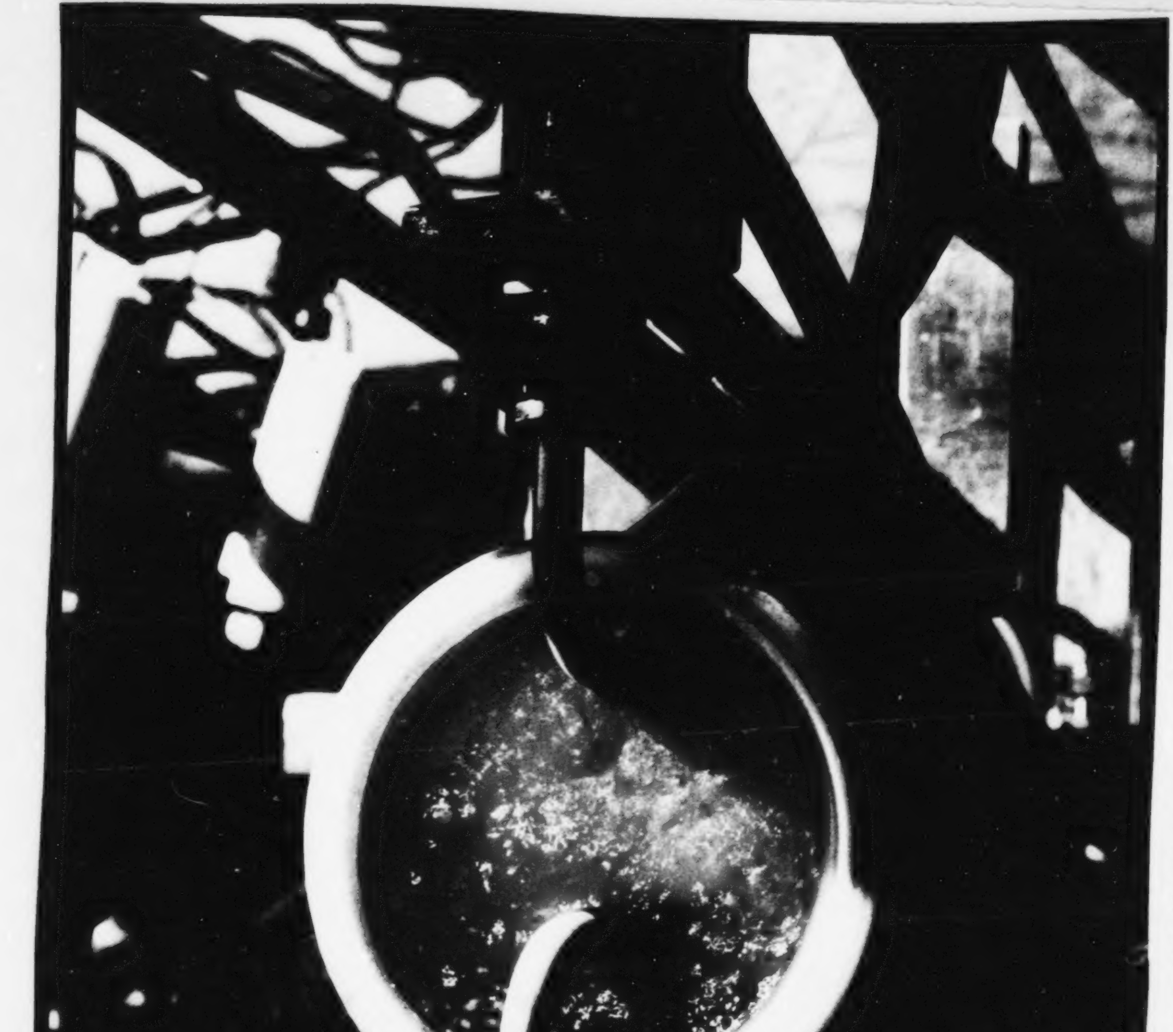


Figure B-8. Photograph of cryogenic U-tube sampling device in sampling position (immersed in LOX).

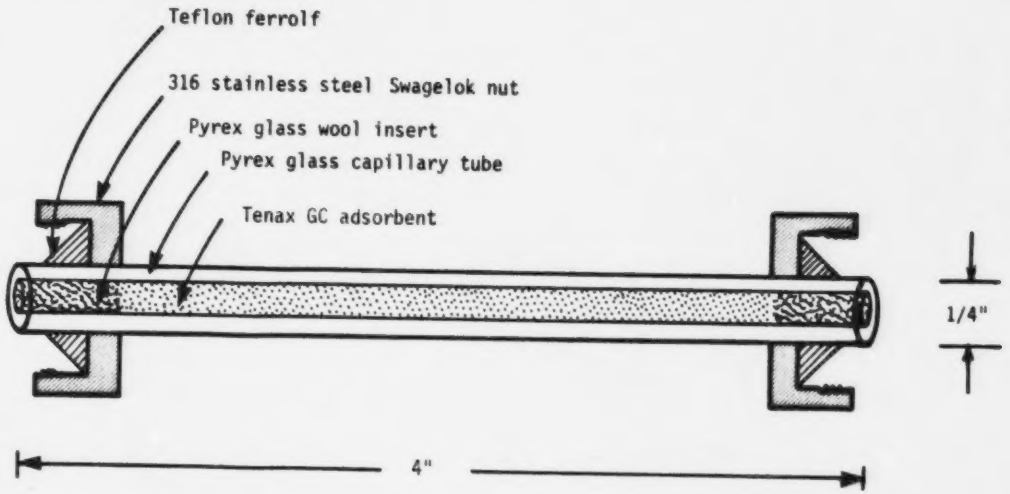

Teflon ferrolf
316 stainless steel Swagelok nut
Pyrex glass wool insert
Pyrex glass capillary tube
Tenax GC adsorbent
1/4"
4"

Figure B-9. Diagram of Tenax trap sampling device.

Sampling with the Tenax traps was conducted in the same manner as described for the cryogenic U-tube traps, except the Tenax traps were operated at ambient temperatures. Also, the sampling duration was increased to approximately 120 min since the Tenax traps are not prone to flow restrictions caused by a buildup of frozen material. Figure B-10 presents a photograph of the Tenax trap sampling device and Smith-Greenburg midget impinger in sampling position.

The XAD-2 sampling device utilized XAD-2 adsorbent resin. The traps were constructed from 5-inch lengths of 1/2-inch O.D. 316 stainless steel tubing. Each end of the tubing was fitted with 1/2-inch to 1/4-inch Swagelok reducing tube unions to connect the trap to the CPA. Prior to packing the tubes with XAD-2 resin, the entire unit was muffled at 400°C for 4 hrs. The traps were then packed with XAD-2 resin, 80/100 mesh, using a small swatch of pyrex glass wool (also muffled) inserted in each end to retain the packing. Figure B-11 presents a diagram of the completed XAD-2 sampling device.

Sampling with the XAD-2 traps was conducted in the same manner as described for the Tenax sampling devices. Figure B-12 presents a photograph of the XAD-2 sampling device and modified Smith-Greenburg Midget Impinger in sampling position.

B.3 ANALYTICAL METHODS AND RESULTS

Samples from the spray pond test site were received on November 25, 1980. The samples were assigned consecutive laboratory identification numbers and stored at 4°C until analyzed.

Analyses were conducted for volatile and semivolatile organics. Volatile organics analyses were based on variations to EPA Method 624. Semivolatile organics (phenols and polynuclear aromatics) analyses were based on sample preparation variation to EPA Method 625 in conjunction with fused silica capillary column GC/MS.

B.3.1 Analysis of Volatile Organics

The analytes of interest were benzene, toluene, and ethylbenzene. The sludge wastewater and Tenax trap samples were analyzed for these components.

Sludge

A 1.0g aliquot of the mixed sludge was weighed into a 15-ml crimp top vial. Pentane (9 ml) and 1-brom-2-chlorpropane (10 μg) were added as internal standards. A 1-μl aliquot of this diluted sample was injected in a 0.2-percent Carbowax 1500 on a Carbopack C packed GC column in a Finnegan 1020 GC/MS instrument. Analysis and quantitation were conducted per EPA Method 624 using the internal standard method.

Quality control for the volatiles analysis entailed the analysis of a method blank and a method standard spiked at 10 μg of sludge.

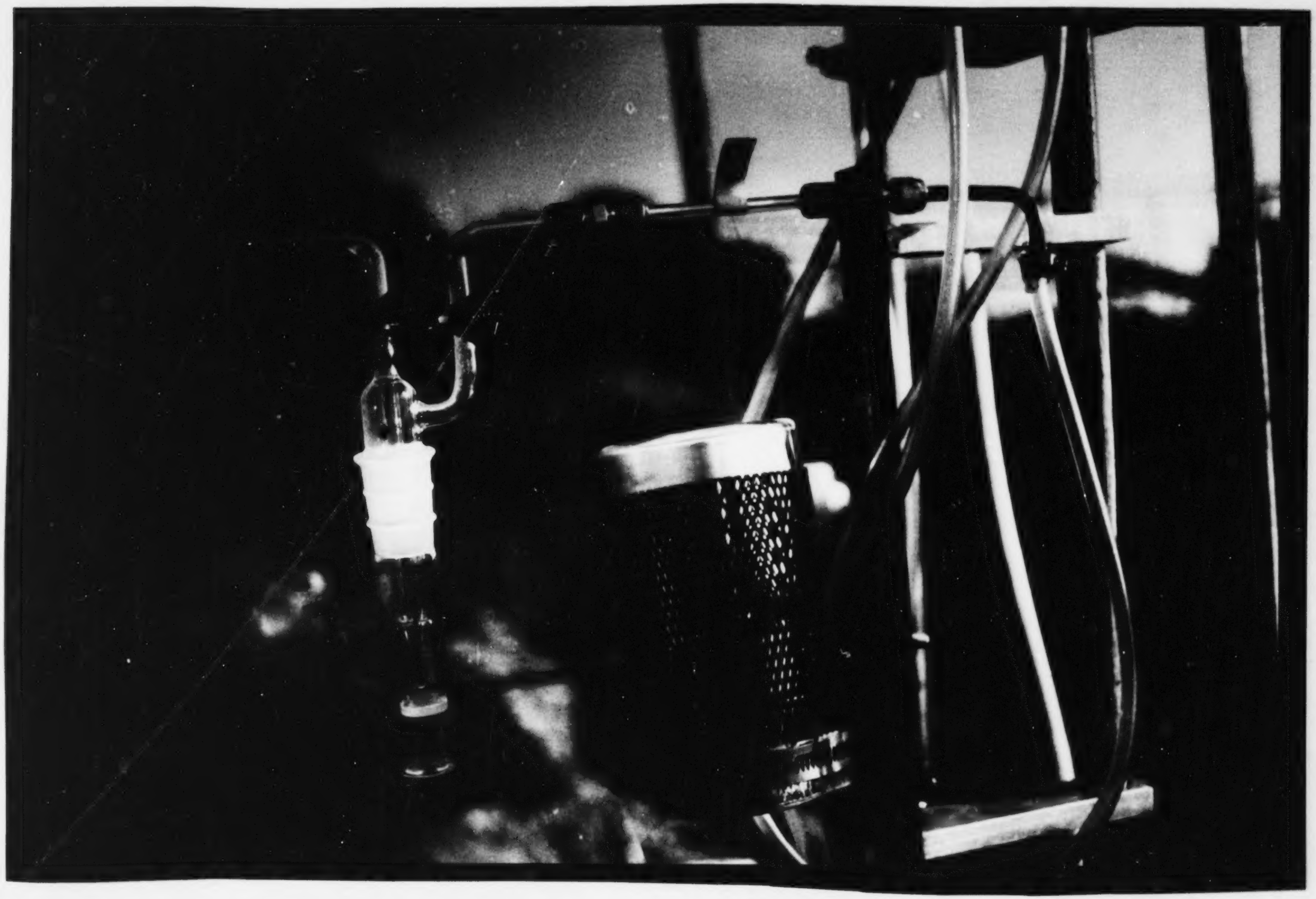


Figure B-10. Photograph of Tenax trap sampling device and modified Smith-Greenburg midget impinger in sampling position.

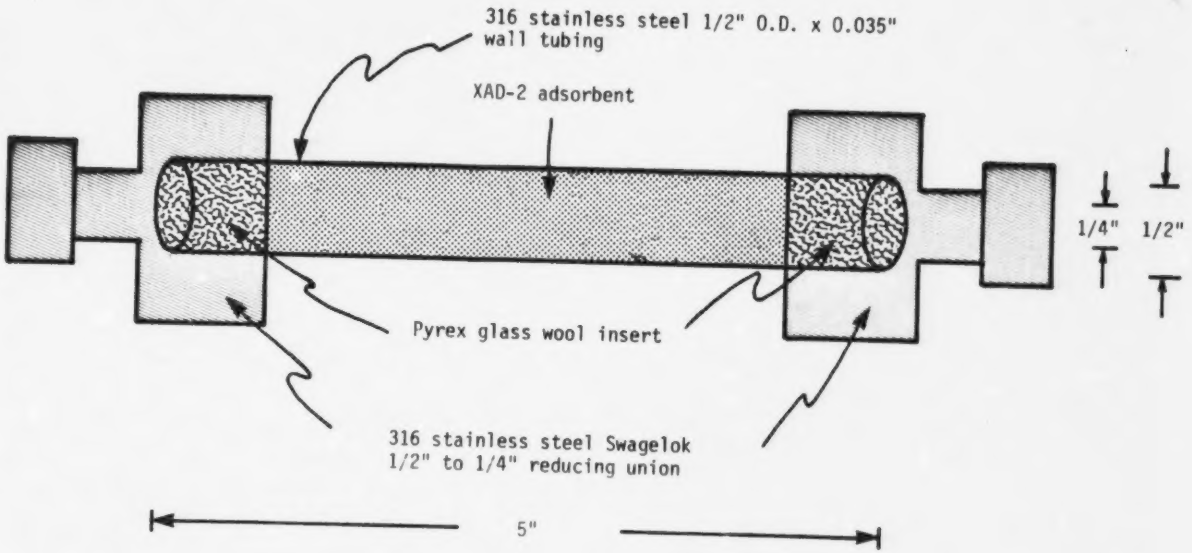

316 stainless steel 1/2" O.D. x 0.035" wall tubing
XAD-2 adsorbent
Pyrex glass wool insert
316 stainless steel Swagelok 1/2" to 1/4" reducing union
5"
1/4"
1/2"

Figure B-11. Diagram of XAD-2 trap sampling device.

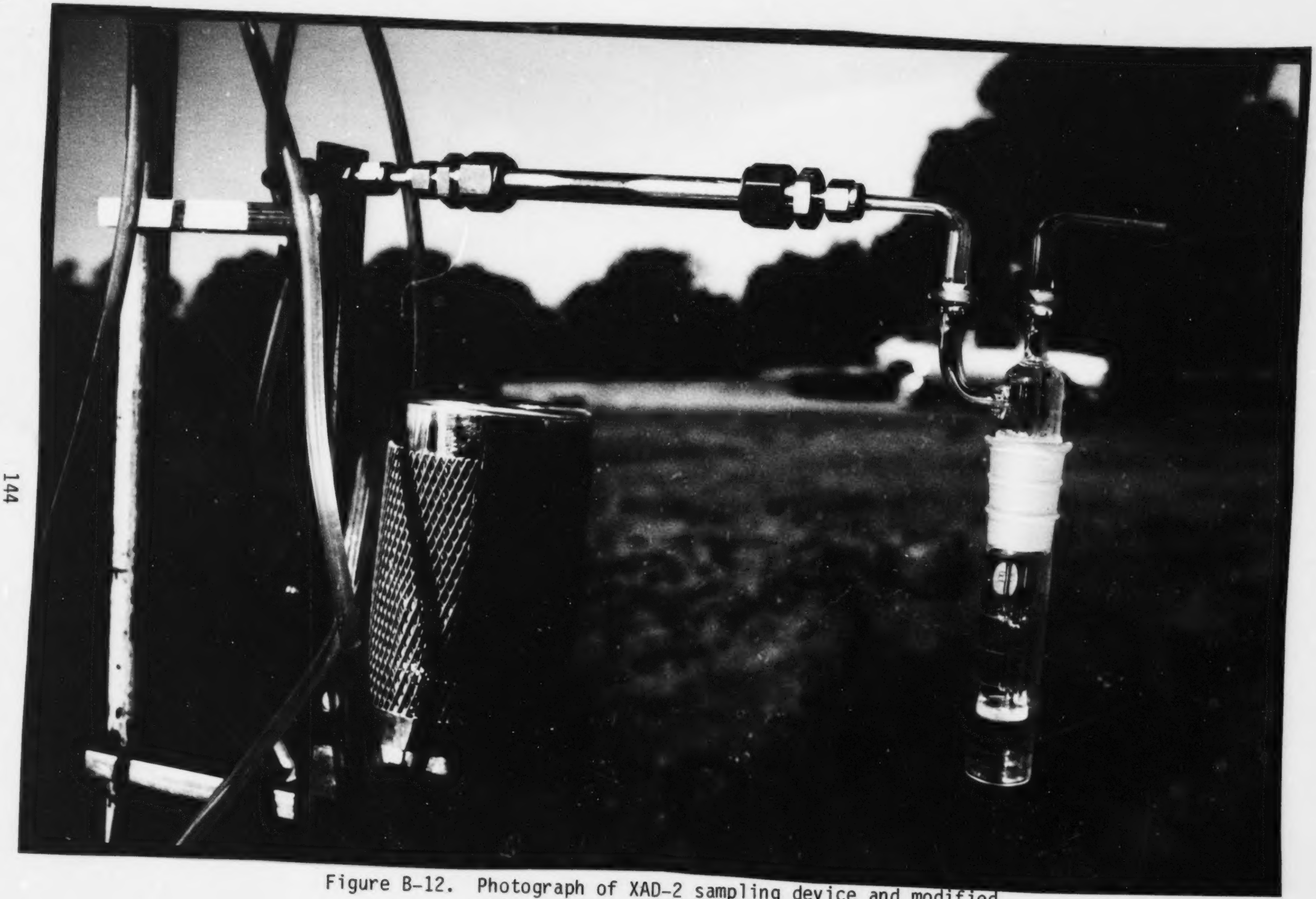


Figure B-12. Photograph of XAD-2 sampling device and modified Smith-Greenburg midget impinger in sampling position.

Water Samples

Water samples were analyzed for volatile organics using EPA Method 624 and 1- to 5-ml samples. The surrogate compounds d_6-benzene and d_8-toluene were added to each sample.

Tenax Traps

Traps were prepared from Tenax GC (Applied Science) in 1/4 x 4 inch glass tubes. Prior to sampling, every trap was spiked with d_6-benzene (100 ng) to index recovery of the trapped samples.

The exposed Tenax trap contents were transferred to the laboratory in the 12 x 1/8 inch stainless steel tubes used in the Tekmar LSC2 purge and trap device. The reassembled traps were purged with helium to remove air and then thermally desorbed for analyses per EPA Method 624.

B.3.2 Analysis of Semivolatile Organics

Semivolatile organics analyzed are listed in Table B-2. These analyses were conducted by variations to EPA Method 625 in the sample preparation and use of fused silica capillary colum GC/MS to determine these compounds.

TABLE B-2. SEMIVOLATILE ORGANICS ANALYZED IN WOOD PRESERVING SAMPLES

Compound	Name
1	Phenol
2	2-Nitrophenol
3	2,4, Dichlorophehol
4	2,4,6 Trichlorophenol
5	4-Nitrophenol
6	4,6-Dinitro-O-cresol
7	Pentachlorophenol
8	Acenaphthene
9	Fluoranthene
10	Naphthalene
11	1,2-Benz(a)anthracene
12	Chrysene
13	Acenaphthylene
14	Phenanthrene
15	Fluorene
16	Pyrene
17	Benzofluoranthenes
18	Benzo(a)pyrene

Sample Preparation

Sludge

The following precedure was ued to prepare sludge samples:

1. Place 10.0g of the sludge in a clean 250-ml brown bottle. Add 10.0g of anhydrous sodium solfate and 100 ml of pesticide grade dichloromethane. Shake occasionally and allow to sit overnight at room temperature.

2. Take 1.0 ml of each extract of GC/FID screening. Store the remaining extract at 4°C.

3. As required by the GC/FID screening, filter the extract into a Kuderna-Danish concentrator and concentrate to 1.0 ml.

The GC/FID screening stage was necessary due to the wide variability of sample concentrations. Figure B-13 summarizes the semivolatile extraction scheme for sludge samples.

XAD-2 Cartridges

The XAD-2 cartridge was carefully opened, any silicone stopcock grease was removed with a CH_2Cl_2 wetted towel, and the contents transferred to a preextracted Soxhlet thimble. The XAD-2 material in the Soxhlet was spike with surrogate mix and extracted overnight with CH_2Cl_2. The extract was concentrated to 1 to 100 ml based on the amount of extractable material present.

Quality control for XAD-2 samples consisted of the analysis of surrogate spikes, field blanks, and spiked method blanks.

Impinger Catches

Midget impinger catches were composited for analysis in the laboratory. Each composite water sample was extracted per EPA Method 625. The extracts were concentrated to 0.5 ml for analysis.

U-Tubes

U-tubes were rinsed into a 0.40-ml vial with dichloromethane. Anhydrous sodium solfate was added to each vial and the vials shaken. The extract was concentrated to 0.5 ml for analysis.

Soils

Soil samples were extracted as follows:

1. Weigh a 50g aliquot into a 250-ml centrifuge bottle. Add surrogate standards.

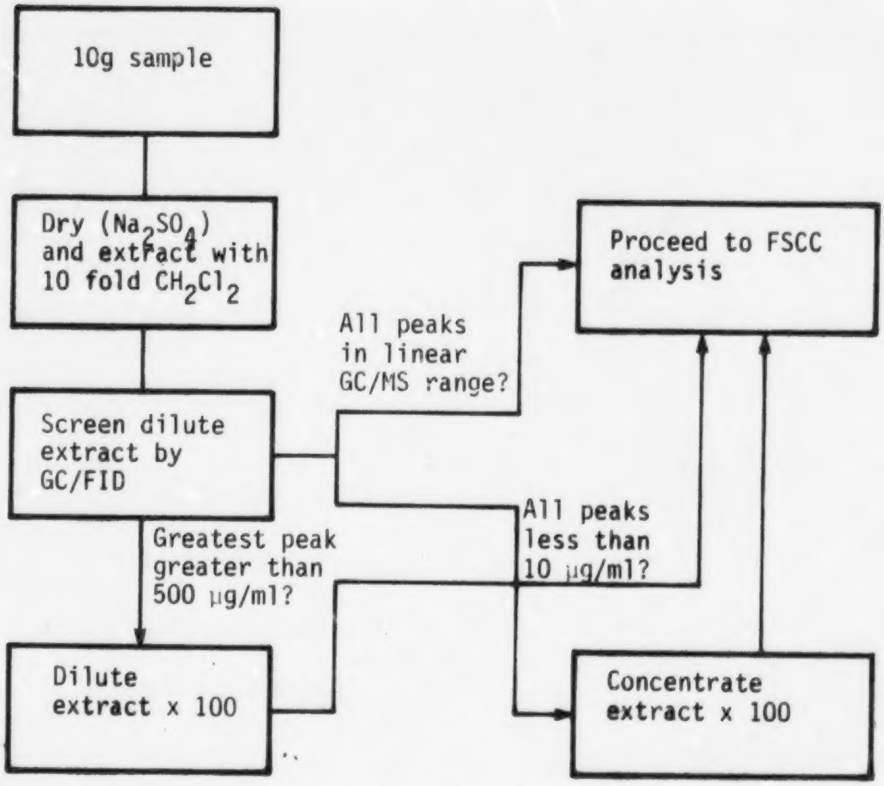

10g sample
Dry (Na_2SO_4) and extract with 10 fold CH_2Cl_2
Screen dilute extract by GC/FID
All peaks in linear GC/MS range?
Proceed to FSCC analysis
All peaks less than 10 μg/ml?
Greatest peak greater than 500 μg/ml?
Dilute extract x 100
Concentrate extract x 100

Figure B-13. Proposed analysis scheme for phenols/PAH s in wood preserving sludges.

2. Adjust the pH of the sample to 12.0 with 6N NaOH.

3. Add approximately 30 ml of water and homogenize for a few seconds. Add 60 ml of methylene chloride, homogenize briefly again, withdraw the homogenizer, and rinse it into the sample with water then with 5 to 10 ml of methylene chloride.

4. Centrifuge the sample aliquot at 1,400 rpm for 5 min to reduce formation of an emulsion layer at the water/methylene chloride interface. Withdraw the extract using a 25-ml Mohr pipet.

5. Perform an additional two extractions by adding 60 ml methylene chloride, homogenizing, and centrifuging as indicated above.

6. Acidify the sample to a pH less than 2 using 6N HCl. Add the acid drop-by-drop with constant mixing to prevent foaming.

7. Extract the sample again as described in Sections 1.3 to 1.6, keeping the addition of water to a minimum.

8. Combine and dry the extracts by passing through a drying column packed with 10 cm of anhydrous Na_2SO_4. Concentrate to a final volume of 1 ml using a Kuderna-Danish apparatus equipped with a calibrated receiver.

Extract Analysis

Each of the extracts obtained as described in the previous section was analyzed for the compounds listed in Table B-2 using fused silica capillary column GC/MS. The instrument operating conditions are listed in Table B-3.

The quality control requirements listed in EPA Method 625 were followed, including analytical calibration, mass spectrometer tuning to meet decafluorotriphenylphosphine (DFTPP) criteria, and the use of the multiple internal standard quantitation method. The internal standards used were d_8-naphthalene, d_{10}-anthracene, and d_{12}-chrysene.

B.3.3 Analytical Results and Discussion

The qualitative results from the spray pond test program are shown below. The sample log which corresponds to this discussion is presented in Table B-4.

U-tubes

Samples A8, A10, A12, A16, A20, A22, A24, and A7 were analyzed for volatiles. Sample A20 contained benzene at 12 ng, toluene at 19 ng, and ethylbenzene at 9 ng. All the others were not detected or less than 5 ng was collected.

TABLE B-3. FUSED SILICA CAPILLARY COLUMN PARAMETERS

Column:	
30m x 0.25m SE-54 WCOT (JaW Scientific)	
Splitless Injection Parameters:	
Injection mode:	Splitless
Sweep initiation:	30 sec
Sweep flow:	±12 ml/min
Column flow (He) Measured at atmospheric:	1.0 ml/min
Interface:	
Temperature:	300°C
Column directly coupled to source (no transfer lines)	
Temperature Program:	
Initial:	30°C for 2 min
Program:	Ramp to 300°C at 10°C/min
Hold:	300°C, 15 min
Mass Spectral Parameters:	
Ionization mode/energy:	Electron impact/70 eV
Total scan time:	1.0 sec
Mass range:	35 to 475 AMU

TABLE B-4. SAMPLE LOG

Sample No.		
1	Impinger No. 1A	
2	Impinger No. 2A	
3	Impinger No. 3A	
4	Impinger No. 4A	
5	Impinger No. 5A	
6	Impinger No. 6A	
7	Mell blank	
1A		
2A		
3A		
4A	LOX test No. 1, 1335 to 1358, 11-18-80	
5A		
6A		
7A	Blank U-tube	
8	Impinger No. 1A (XAD-2 B-1)	
9	Impinger No. 2A (Tenax C-1)	
10	Impinger No. 3A (XAD-2 B-2)	
11	Impinger No. 4A (Tenax C-2)	
12	Impinger No. 5A (XAD-2 B-3)	
13	Impinger No. 6A (Tenax C-3)	
B-1		
B-2	Xad-2 cartridge, Run No. 1, 11-18-80	
B-3	1502 to 1717	
C-1		
C-2	Tenax Trap, Run No. 1, 11-18-80	
C-3		
C-4	(Bottom)	
C-5		
C-6	Tenax Trap, Run No. 3, 11-19-80	
C-7		
C-8		
C-9	(Top)	
14	Impinger rinse 1A	
15	Impinger rinse 2A	
16	Impinger rinse 3A	Impinger contents, test No. 3
17	Impinger rinse 4A	11-19-80 (Tenax)
18	Impinger rinse 5A	
19	Impinger rinse 6A	
20	Mell blank	11-19-80
21	Impinger rinse 2B	
22	Impinger rinse 2B	
23	Impinger rinse 3B	Impinger contents, test No. 3
24	Impinger rinse 4B	11-19-80 (Tenax)
25	Impinger rinse 5B	
26	Impinger rinse 6B	

TABLE B-4. Continued

Sample No.		
A8	U-tube (Bottom)	
A9	U-tube	
A10	U-tube	Test No. 4, 11-19-80
A11	U-tube	1147 to 1317
A12	U-tube	
A13	U-tube (Top)	
A14	U-tube (Bottom)	
A15	U-tube	
A16	U-tube	Test No. 5, 11-19-80
A17	U-tube	1425 to 1508
A18	U-tube	
A19	U-tube (Top)	
27	Impinger rinse 1B (Bottom)	
28	Impinger rinse 2B	
29	Impinger rinse 3B	Impinger contents, test No. 5
30	Impinger rinse 4B	11-19-80
31	Impinger rinse 5B	
32	Impinger rinse 6B (Top)	
33	Impinger rinse 1B (Bottom)	
34	Impinger rinse 2B	
35	Impinger rinse 3B	Impinger contents, test No. 6
36	Impinger rinse 4B	11-19-80
37	Impinger rinse 5B	
38	Impinger rinse 6B (Top)	
B4	XAD-2 (Bottom)	
B5	XAD-2	
B6	XAD-2	Test No. 6, 11-19-80
B7	XAD-2	1536 to 1645
B8	XAD-2	
B9	XAD-2 (Top)	
39	Impinger rinse 1B	
40	Impinger rinse 2B	
41	Impinger rinse 3B	Impinger contents, test No. 7
42	Impinger rinse 4B	
43	Impinger rinse 5B	
44	Impinger rinse 6B	
45	No sample	
B10	XAD-2 (Bottom)	
B11	XAD-2	
B12	XAD-2	Test No. 8, 11-20-80
B14	XAD-2	0811 to 1111
B15	XAD-2	
45	Impinger rinse B1	
46	Impinger rinse B2	
47	Impinger rinse B3	Test No. 8, 11-20-80

TABLE B-4. Continued

Sample No.		
48	Impinger rinse B4	
49	Impinger rinse B5	
50	Impinger rinse B6	
B16	XAD-2 (Top)	Test No. 9, 11-20-80 1137 to 1237
B17	XAD-2 (Bottom)	
B18	XAD-2	
B19	XAD-2	
B20	XAD-2	
B21	XAD-2	
B22	XAD-2 (Top)	
51	Impinger rinse 1B	
52	Impinger rinse 2B	
53	Impinger rinse 3B	
54	Impinger rinse 4B	
55	Impinger rinse 5B	
56	Impinger rinse 6B	
C10	Tenax Trap (Bottom)	Test No. 10, 11-20-80 1319 to 1521
C11	Tenax Trap	
C12	Tenax Trap	
C13	Tenax Trap	
C14	Tenax Trap	
C15	Tenax Trap (Top)	
57	Impinger rinse (Bottom)	Test No. 10, 11-20-80
58	Impinger rinse	
59	Impinger rinse	
60	Impinger rinse	
61	Impinger rinse	
62	Impiger rinse (Top)	
63	Impinger rinse (Bottom)	Test No. 11, 11-20-80
64	Impnger rinse	
65	Impinger rinse	
66	Impinger rinse	
67	Impinger rinse	
68	Impinger rinse (Top)	
C16	Tenax Trap (Bottom)	Test No. 11, 11-20-80 1544 to 1744
C17	Tenax Trap	
C18	Tenax Trap	
C19	Tenax Trap	
C20	Tenax Trap	
C21	Tenax Trap (Top)	
C22	Tenax blank	
C23	Tenax blank	
B26	XAD-2 blank	
B29	XAD-2 blank	

TABLE B-4. Concluded

Sample No.	
	Sample Log -- Wastewater and Sludge
100	Pond sludge 11-2-80 (0830)
101	Pond sludge 11-2-80 (0830)
102	Pond sludge 11-2-80 (0830)
103	Pond wastewater (pump discharge) 11-2-80 (0830)
104	Pond wastewater (pump discharge) 11-2-80 (0830)
105	Pond wastewater (pump discharge) 11-2-80 (0830)
106	Sludge spray pond 11-19-80 (1215)
107	Pond grab sample (surface) 11-19-80 (1015)
108	Pond wastewater (pump discharge) 11-19-80 (1045)
109	Pond sludge (5 ft from edge 11-19-80 (1215)
110	Farmers pond (bottom core sample) 11-19-80 (1000)
111	Farmers pond (behind RR tracks) 11-19-80 (0145)
112	Farmers field (3-part core soil sample) 11-19-80 (1050)
2 x 113	Farmers pond VOA
2 x 114	Pond VOA (pump discharge) 11-19-80 (1045)
2 x 115	Pond VOA (surface water) 11-20-80 (0820)
116	Floc tank sludge to drying bed — 1-19-80 Plant D
117	Aeration tank afer floc tank -- 1-19-80 Plant D
118	Condenser pond before floc tank — 1-19-80 Plant D
119	Condenser pond VOA Plant D
120	Aeration tank VOA Plant D
121	Sludge VOA Plant D
2 x 122	Wastewater from separator 11-20-80 (0930) PCP
2 x 123	Wastewater before pond 11-20-80 (0910)

Samples A9, A11, A13, A19, A1, A6, A21, A23, and A25 were analyzed for phenols and polynuclear aromatics. All results except for the following were negative. The detection limit was 1 μg collected for all samples.

Sample	A9	A11	A1
Pentachlorophenol	41	5.2	4.0
Fluoranthene	1.4	1	1
Pyrene	1.1	1	1
Phenanthrene	1.7	1	1

Figure B-14 is a representative chromatogram from a U-tube extract.

XAD Cartridges

Samples B1, B2, B3, B5, B7, B9, B11, B14, B16, B18, B20, B22, B26, and B29 were extracted and analyzed for phenols and polynuclear aromatics. No compounds were detected to a detection limit of 1 μg. The detection limit for naphthalene in these samples is 10 μg due to a minor contamination of the XAD-2. Figures B-15 and B-16 compare the chromatograms from an XAD-2 blank and a sample.

Tenax Traps

All Tenax traps C1 through C23 were analyzed for benzene, toluene, and ethylbenzene. These compounds were not detected in any samples. Due to a low level of Tenax contamination, the detection limits were 0.7 μg for each of these compounds.

Waters, Sludges, and Soils

These samples were analyzed for volatile aromatics, phenols, and polynuclear aromatics as listed in Tables B-5 and B-6. Figure B-17 is a typical chromatogram for a volatiles analysis. Figure B-18 is a chromotogram for a pond sludge extract.

The composite pond water sample (Field I.D. 103+104+105 and lab I.D. 80-11-043-83) was also analyzed for oil and grease by standard methods. The measured value was 160 μg/l.

Impinger Catches

Impinger catch samples were composited as follows:

- Sample 1 - Sample 6
- Sample 7 + Sample 20

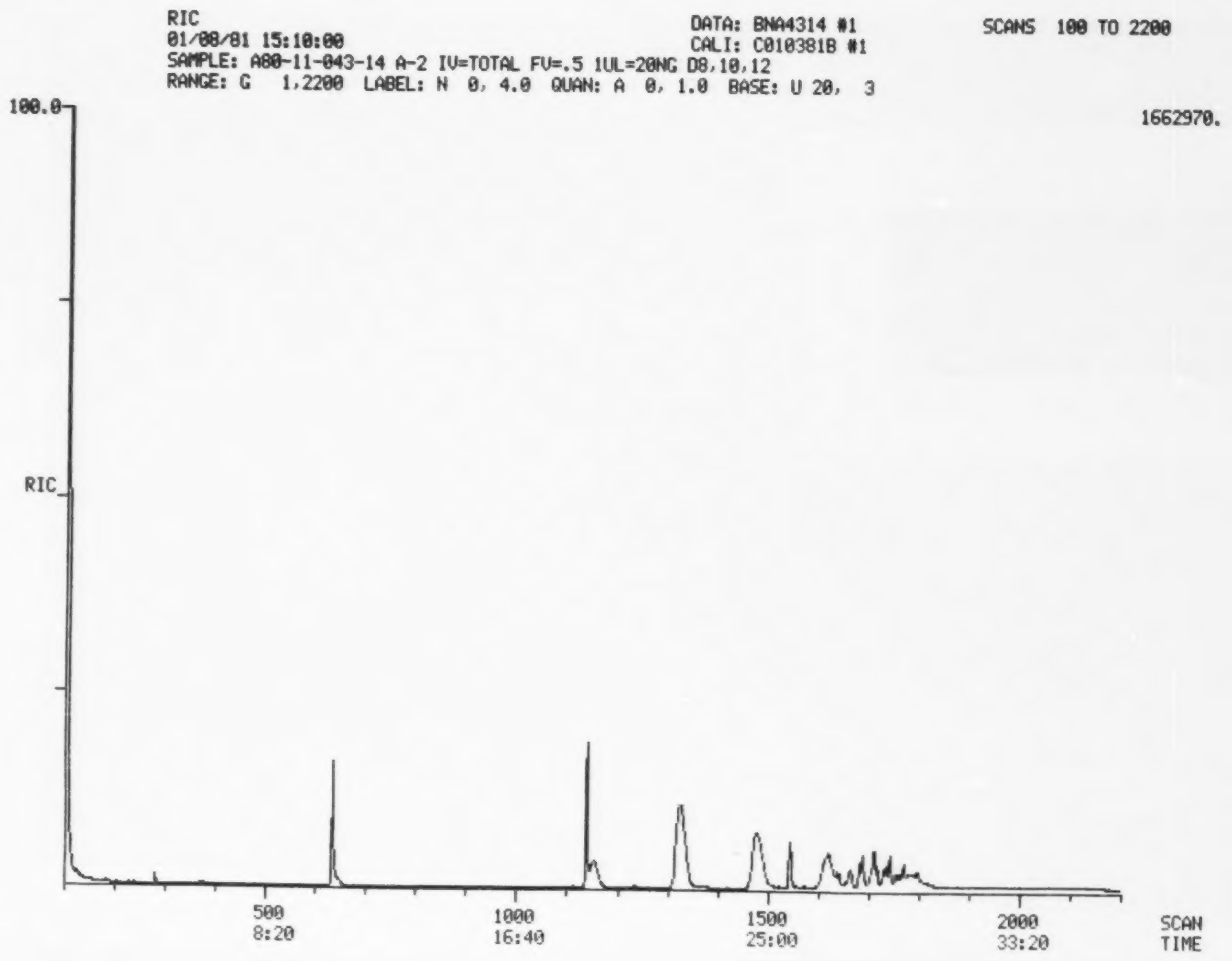


Figure B-14. Total ion current chromatogram U-tube extract.

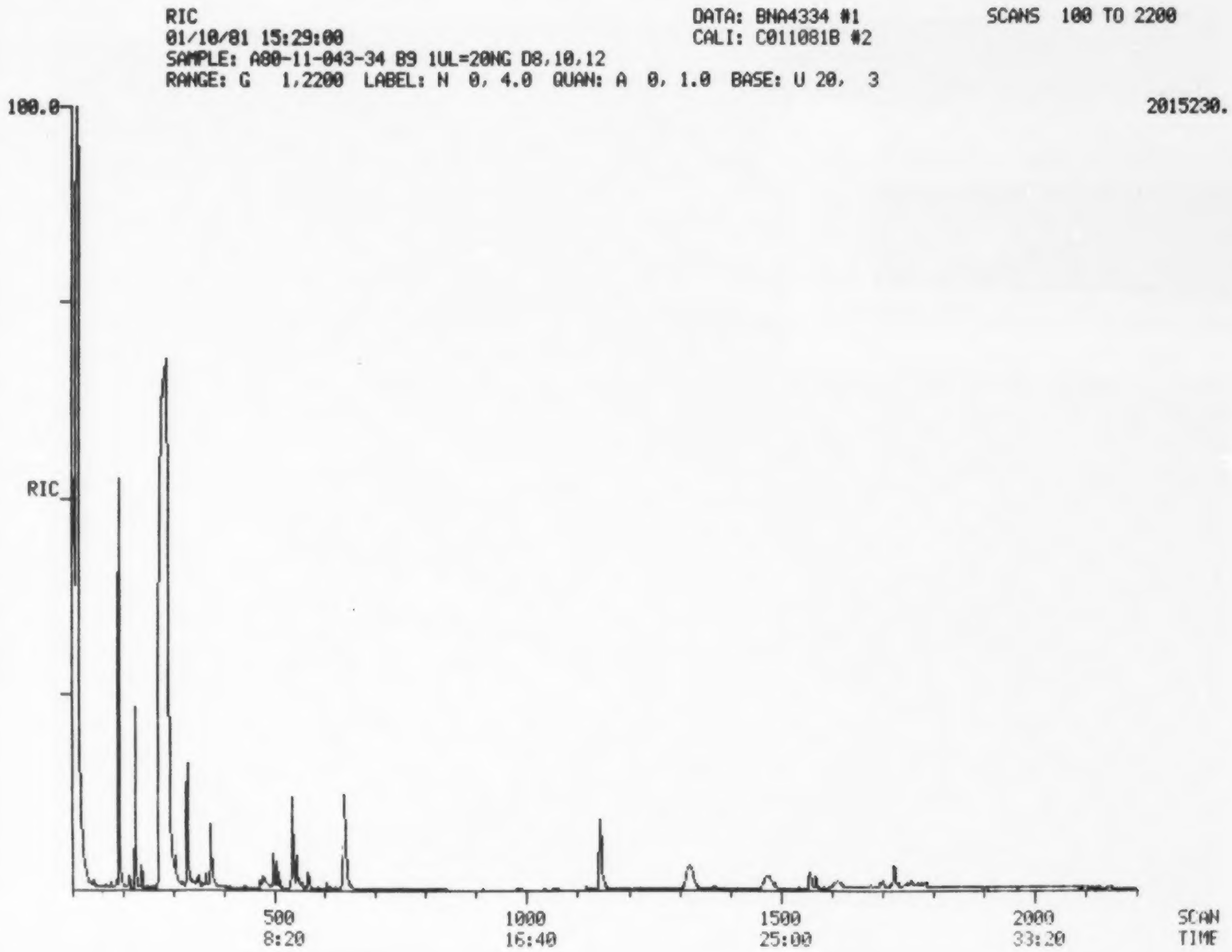


Figure B-15. Chromatogram from XAD-2 sample.

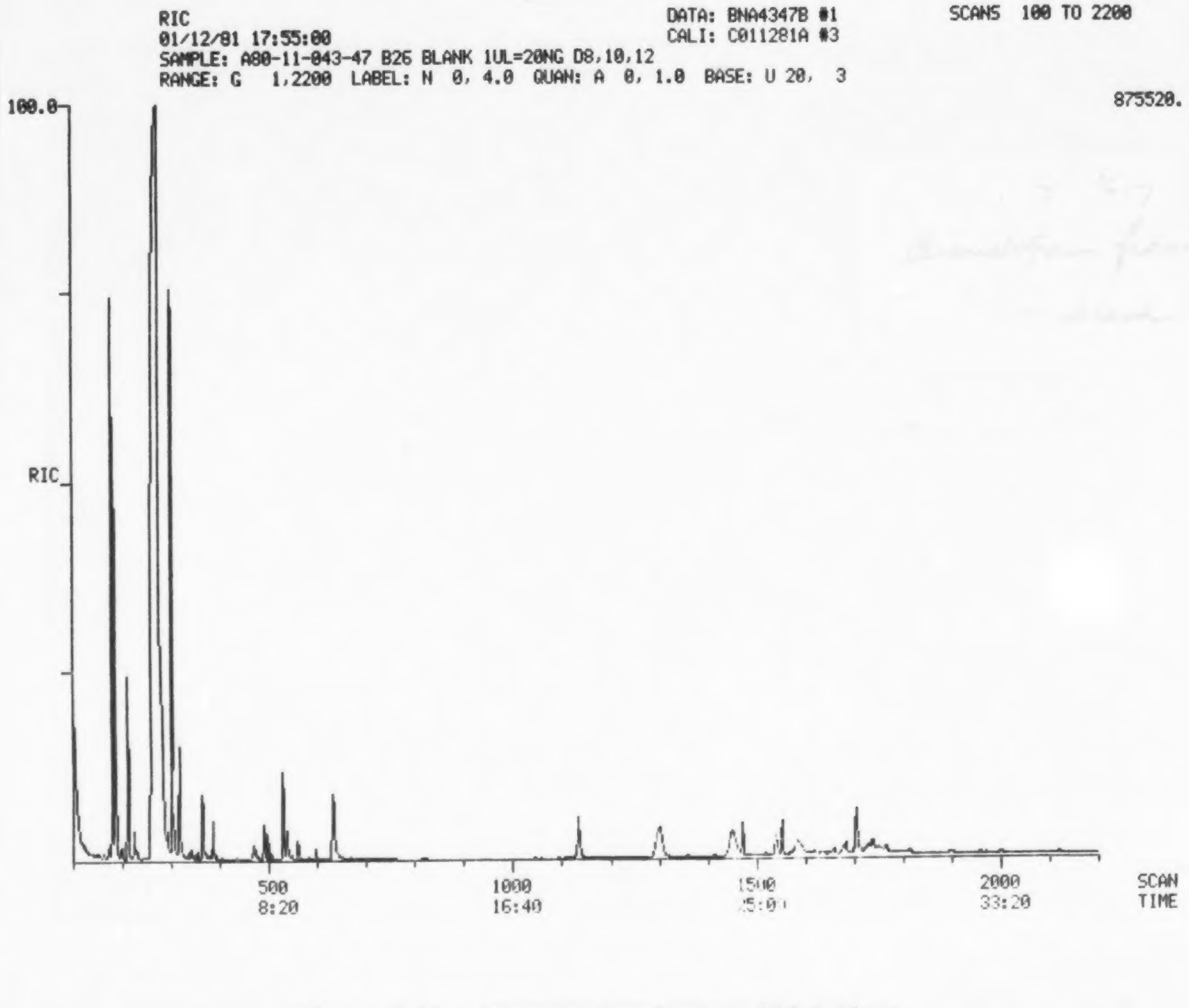


Figure B-16. Chromatogram from an XAD-2 blank.

TABLE B-5.

WOOD PRESERVING TEST RESULTS TEST Spray Pond Samples

TEST SITE: TEST DATE

COMPOUND Acurex I.D. # A80-11-043	100-102+109 -80	103-105 -83	107 -87	108 -88
Description	Composite sludge	Comp.Water	Pond Water	Pond At Pump
Pentachlorophenol	15,000	15	2.2	16
Phenol	<50	<0.1	<0.1	<0.1
Fluoranthene	5800	3.0	5.7	2.7
Naphthalene	1500	4.0	6.3	2.3
Benzo(a)anthracene	2600	0.4	1.4	4.5
Benzo(a)pyrene	20	<0.1	0.1	<0.1
Benzofluoranthenes	87	0.1	0.5	0.1
Chrysene	2000	0.6	1.6	6.2
Acenaphthylene	230	0.1	0.3	0.1
Anthracene	1700	0.7	1.6	0.7
Benzo(ghi)perylene	67	<0.1	<0.1	<0.1
Fluorene	5600	1.7	3.7	2.0
Phenanthrene	9000	6.4	12	7.4
Dibenzo(a,h)anthracene	<50	<0.1	<0.1	<0.1
Indeno(1,2,3-cd)pyrene	85	<0.1	<0.1	<0.1
Pyrene	4400	1.6	2.9	1.1
Benzene	NA	NA	NA	NA
Toluene	NA	NA	NA	NA
Ethylbenzene	NA	NA	NA	NA

All concentrations in units of micrograms per gram except for XAD collections which are total milligrams collected.

TABLE B-6.

WOOD PRESERVING TEST RESULTS

TEST SITE: Alabama

TEST Spray Pond

TEST DATE

COMPOUND				
Field I.D.	122	123	114	115
Acurex I.D. # A80-11-043	-97	-98	-100	-101
Description	Wastewater	Wastewater	Spray Pond	Pond Pump
Pentachlorophenol	790	1160	NA	NA
Phenol	17	48		
Fluoranthene	41	23		
Naphthalene	66	120		
Benzo(a)anthracene	<10	<10		
Benzo(a)pyrene	<10	<10		
Benzofluoranthenes	<10	<10		
Chrysene	<10	<10		
Acenaphthylene	<10	<10		
Anthracene	<10	17		
Benzo(ghi)perylene	<10	<10		
Fluorene	58	22		
Phenanthrene	24	67		
Dibenzo(a,h)anthracene	<10	<10		
Indeno(1,2,3-cd)pyrene	<10	<10		
Pyrene	21	15		
Benzene	NA	NA	0.015	0.015
Toluene	NA	NA	<0.005	0.040
Ethylbenzene	NA	NA	<0.005	<0.005

All concentrations in units of micrograms per gram except for XAD collections which are total milligrams collected.

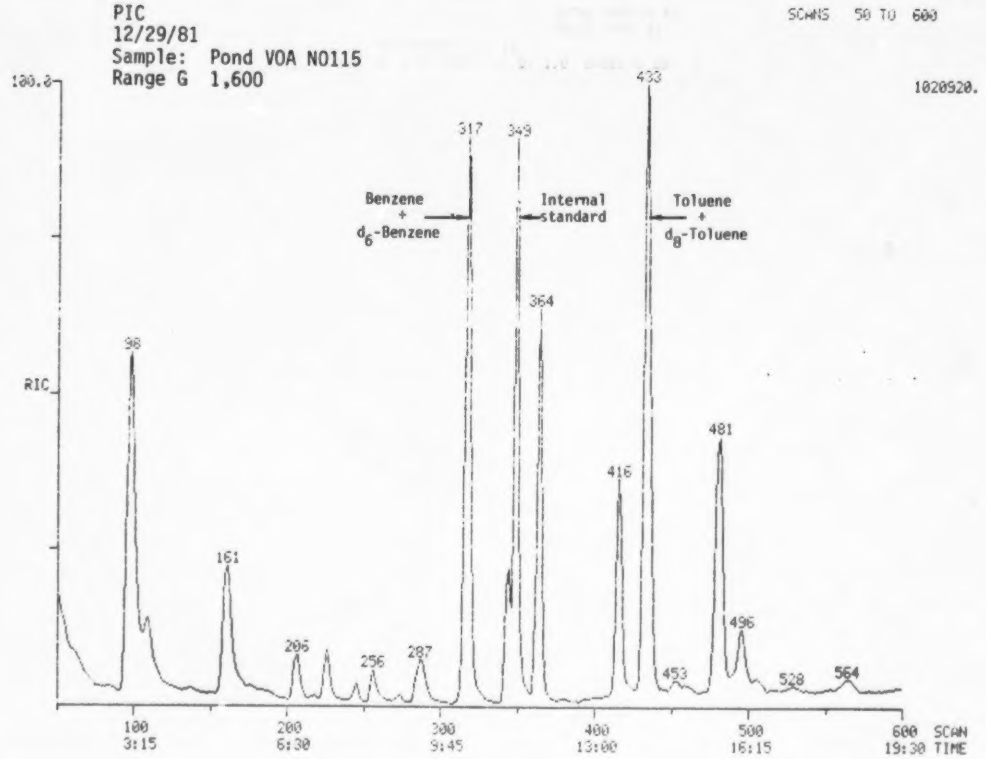


Figure B-17. Volatile analysis chromatogram.

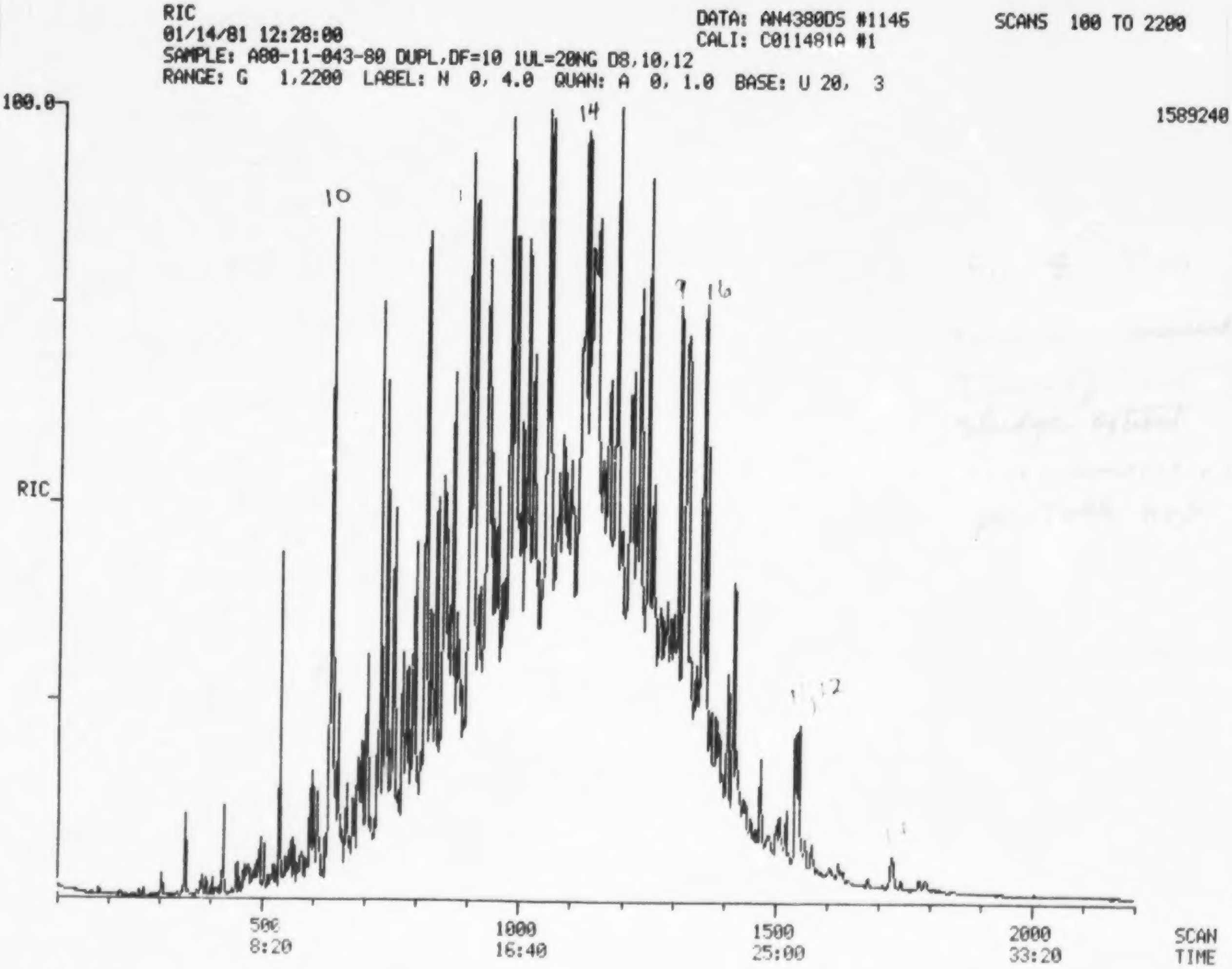


Figure B-18. Total ion current trace of pond sludge extract.

- Sample 8 - Sample 13
- Sample 14 - Sample 19
- Sample 21 - Sample 26

Each of these composite samples was concentrated and analyzed for phenols and semivolatiles. No compounds were measured at the detection limit of 1 μg. Figure B-19 is a chromatrogram of a typical impinger extract.

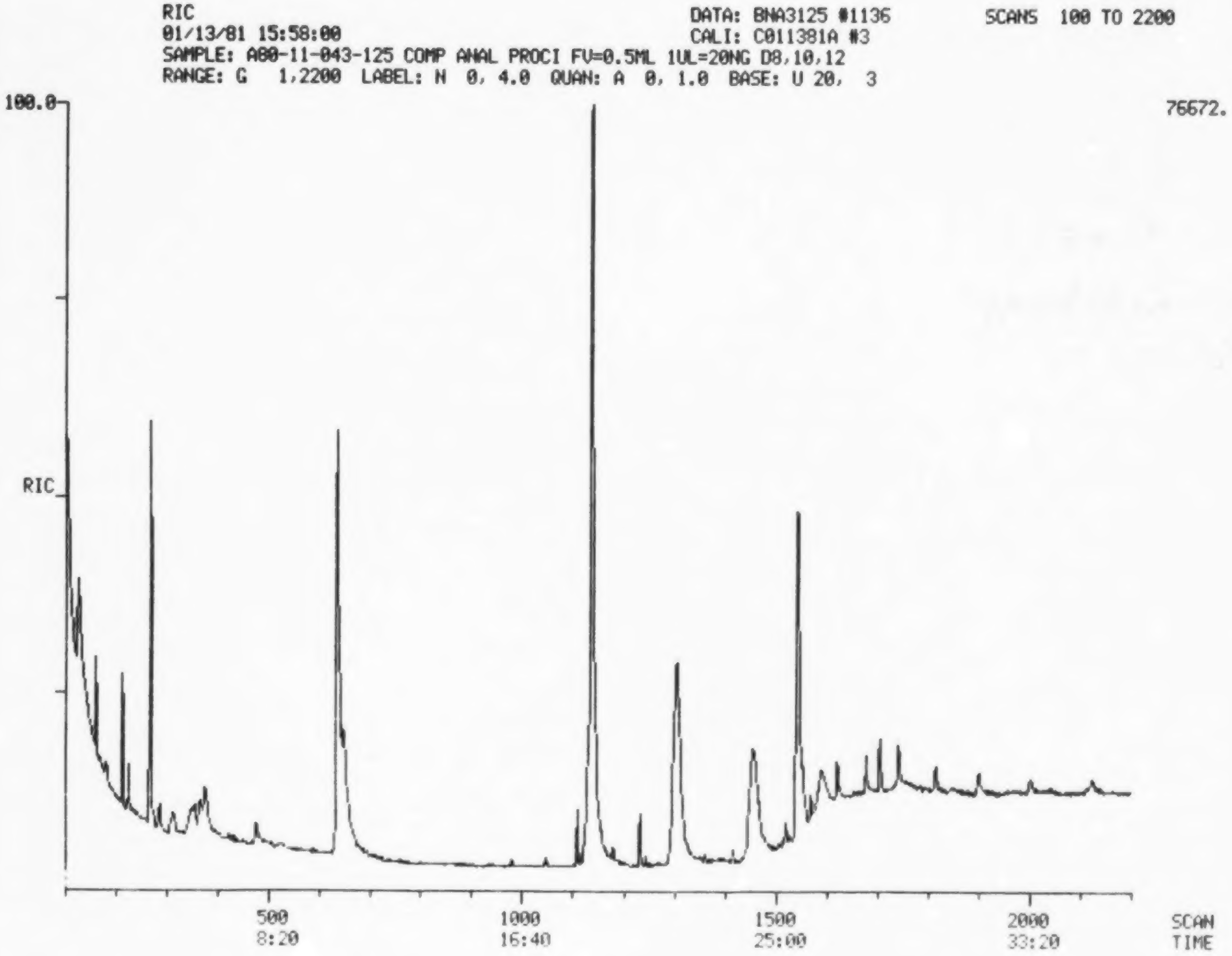


Figure B-19. Typical chromatogram of an impinger extract.

APPENDIX C

CHARACTERIZATION OF EMISSIONS AND RESIDUES FROM THE DISPOSAL OF WOOD PRESERVING WASTES IN NONFOSSIL FUEL BOILER

The handwritten raw data for this study has been compiled and is available upon request. That data covers preliminary and isokinetic source emission sampling, total hydrocarbon determination, and specific low-molecular- weight hydrocarbon determinations. Copies may be obtained from EPA-IERL-Ci 26 W. St. Clair Street, Cincinnati, OH 45268 (513/684-4227).

The scope of this program focused on the gaseous emissions discharged from the stack, and the ash streams which result during combustion and pollution control.

Material balance estimates were difficult since ash and fuel flowrates were not metered by the operator. Estimates were made of each stream and the appropriate material balance evaluation of the destruction and removal efficiency performed (See Section 7).

C-1. TEST SITE

Table C-1 presents a summary of the total production during the field test period.

TABLE C-1. SUMMARY OF TREATED WOOD PRODUCTION FOR THE PERIOD JULY 21 THROUGH JULY 25, 1980

Treatment Product	Penta heavy oil		Penta light oil		Creosote		CCA*		Fire retardant**	
	m^3	ft^3	m^3	ft^3	m^3	ft^3	m^3	ft^3	m^3	ft^3
Utility Poles	255	7962			76.8	2712	1.0	37		
Pilings	30.8	1088			199	7044	11.3	400		
Lumber	12.5	440	52.7	1860	49.6	1753	186	6583	48.6	1717
Plywood									27.2	962

*CAA = Copper chromate arsenate (waterborne)
**Waterborne formulation

C.2 FIELD TEST PROGRAM

The sampling program and collection matrix is presented in section 7 and Table 7-1. The following subsections describe the equipment and techniques employed during sampling.

C.2.1 Preliminary Measurements

Preliminary gas characteristics were determined using EPA Methods 1 through 4 (Federal Register, Volume 42, No. 160, August 18, 1977). Using these criteria, the required number of sampling points was established. With the boiler operating under normal load conditions, two traverses were conducted at right angles to one another on the south stack (No. 2). Figure C-1 presents a schematic of the stack cross section and traverse point locations. Gas velocity measurements were taken using a calibrated 6-ft S-type pitot tube connected to a 0- to 1-inch Magnehelic Series 200 gauge manufactured by Dwyer Instruments Company, Michigan City, Indiana. Exit gas temperatures were measured using a Chromel-Alumel (Type K) thermocouple and a digital thermal indicator manufactured by Doric Incorporated. Table C-2 presents a summary of the velocity/temperature profile data.

TABLE C-2. SUMMARY OF VELOCITY/TEMPERATURE PROFILE DATA FOR SOUTH STACK

	South port				East port			
	ΔP H_2O		Temperature		ΔP H_2O		Temperature	
Location	cm	inches	C^o	F^o	cm	inches	C^o	F^o
1	.99	0.39	120	248	1.42	0.56	142	290
2	1.30	0.51	131	268	1.09	0.43	142	290
3	1.40	0.55	141	286	1.37	0.54	159	319
4	1.50	0.59	163	325	1.52	0.60	174	346
5	1.55	0.61	168	335	1.65	0.65	181	357
6	1.65	0.65	174	345	1.80	0.71	180	355
7	1.63	0.64	175	347	1.88	0.74	182	359
8	1.63	0.64	177	351	1.90	0.75	183	362
9	1.52	0.60	178	353	1.88	0.74	184	363
10	1.35	0.53	180	355	1.73	0.68	184	364

Sampling Locations

Traverse Point Number		Location from Inside Stack Wall
South Port	East Port	
1	11	3/4
2	12	2-7/6
3	13	4-3/16
4	14	6-3/4
5	15	10-1/4
6	16	19-3/4
7	17	23-3/16
8	18	25-5/8
9	19	27-1/2
10	20	29-3/16

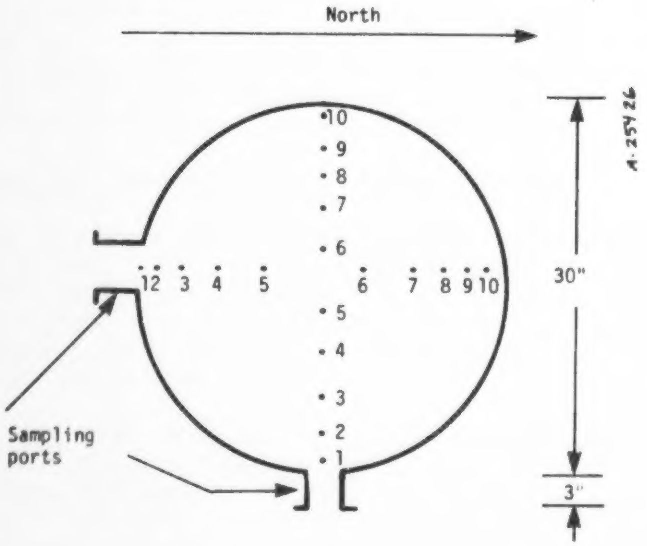

North
10
9
8
7
6
1 2 3 4 5 6 7 8 9 10
5
4
3
2
1
30"
3"
Sampling ports
A-25426

Figure C-1. Schematic of traverse point locations, south stack, no. 2.

Preliminary gas moisture content was calculated using polychrometric data. Successive moisture values, as determined during the actual test runs, then were used to update the preliminary calculated values. Exit gas molecular weight was dtermined by standard orsat analysis before and after each test run. The raw data collected in the field are not presented in this report, but can be obtained as described above.

C.2.2 Isokinetic Source Sampling of Boiler Flue Gas

Sampling of high-molecular-weight organic emissions from the outlet stack was performed using the EPA Method 5 isokinetic sampling train as shown in Figure C-2. The train consists of an in-stack filter, a heated glass-lined probe, an XAD-2 polymer sorbent trap and impingers. The first impinger, a modified Greenburg-Smith (without an impaction plate), was empty, followed by an XAD-2 polymer sorbent trap and a Greenburg-Smith impinger charged with 100 ml of 30-percent hydrogen peroxide. The third impinger was also an empty modified Greenburg-Smith, followed by a silicon dioxide drying trap to protect the vacuum pump and sampling module from moisture. Figure C-3 presents a photograph of the sampling train in sampling position on the south stack.

For each isokinetic source test, a sample was drawn from the fan outlet (at a predetermined constant velocity point) through a probe fitted with the appropriately sized nozzle. Four complete sets of samples were collected. All sampling was conducted during normal boiler operation. Table C-3 presents a summary of the pertinent isokinetic source test parameters.

At the completion of source sampling, the sample train and probes were transported to a field laboratory. Samples were transferred from the sample trains to specially cleaned and labeled storage containers. The probe nozzle, probe, and connecting lines were cleaned also and recovered samples were transferred to the appropriate storage containers. Immediately following sample recovery, all samples were iced in the field and maintained under those conditions during transport to the analytical laboratory.

C.2.3 Total Hydrocarbon Determination of Boiler Flue Gas

A Model 400 total hydrocarbon analyzer (THC) manufactured by Beckman Instruments of Fullerton, California, was used to continuously monitor total hydrocarbons in the sampled gas stream at the south stack. This analyzer uses the flame ionization detection (FID) method. The analyzer output was recorded using a Model 585 strip chart recorder manufactured by Linear Instruments Corporation, Irvine, California.

The FID was operated using zero grade 1.0 hydrogen fuel and zero grade air supplied by Airco Industrial Gases, Santa Clara, California. Hydrogen fuel and zero air pressure were set at 207 kPa (30 psi) and 104 kPa (15 psi), respectively, using internal differential pressure regulators in the analyzer.

Sampling was conducted using the system shown in Figure C-4. The gas sample was extracted from the stack via a 7-micron, sintered, stainless steel Model No. SS-4 FE-7 filter manufactured by Nupro Valve Company of Willoughby,

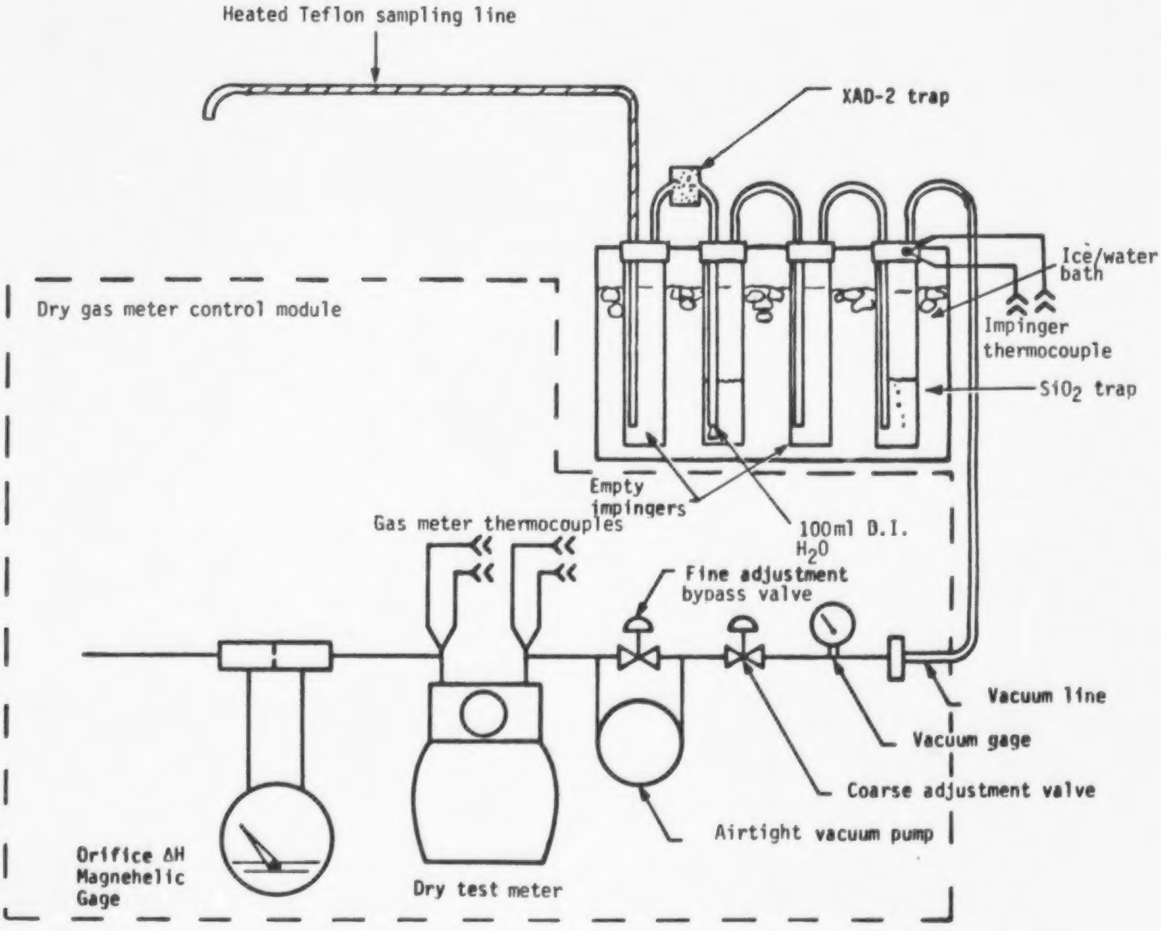

Heated Teflon sampling line
XAD-2 trap
Ice/water bath
Impinger thermocouple
SiO_2 trap
Dry gas meter control module
Empty impingers
100ml D.I. H_2O
Gas meter thermocouples
Fine adjustment bypass valve
Vacuum line
Vacuum gage
Coarse adjustment valve
Airtight vacuum pump
Orifice ΔH Magnehelic Gage
Dry test meter

Figure C-2. Schematic diagram of an XAD-2 high-molecular-weight mass particulate sampling train.

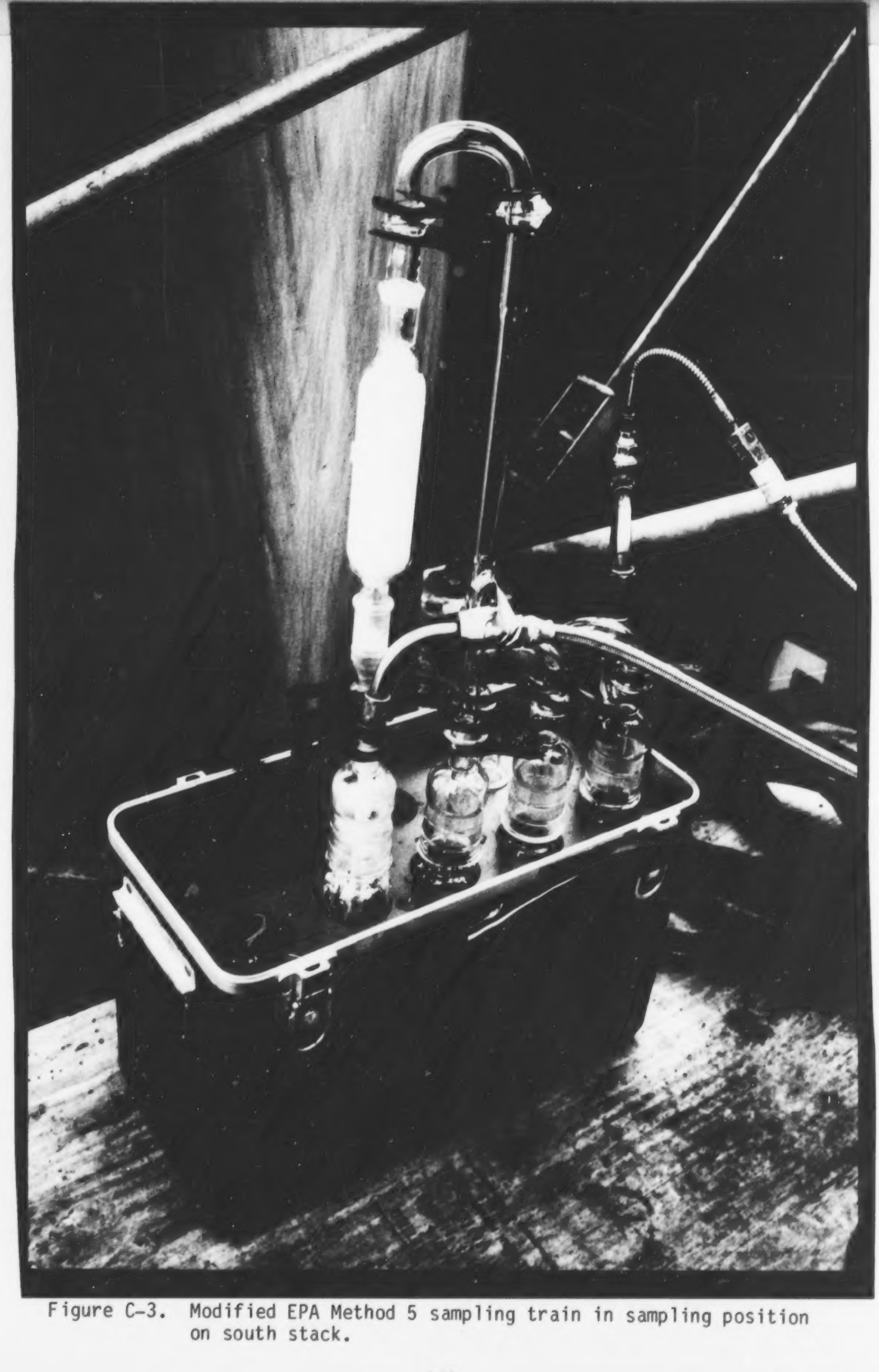


Figure C-3. Modified EPA Method 5 sampling train in sampling position on south stack.

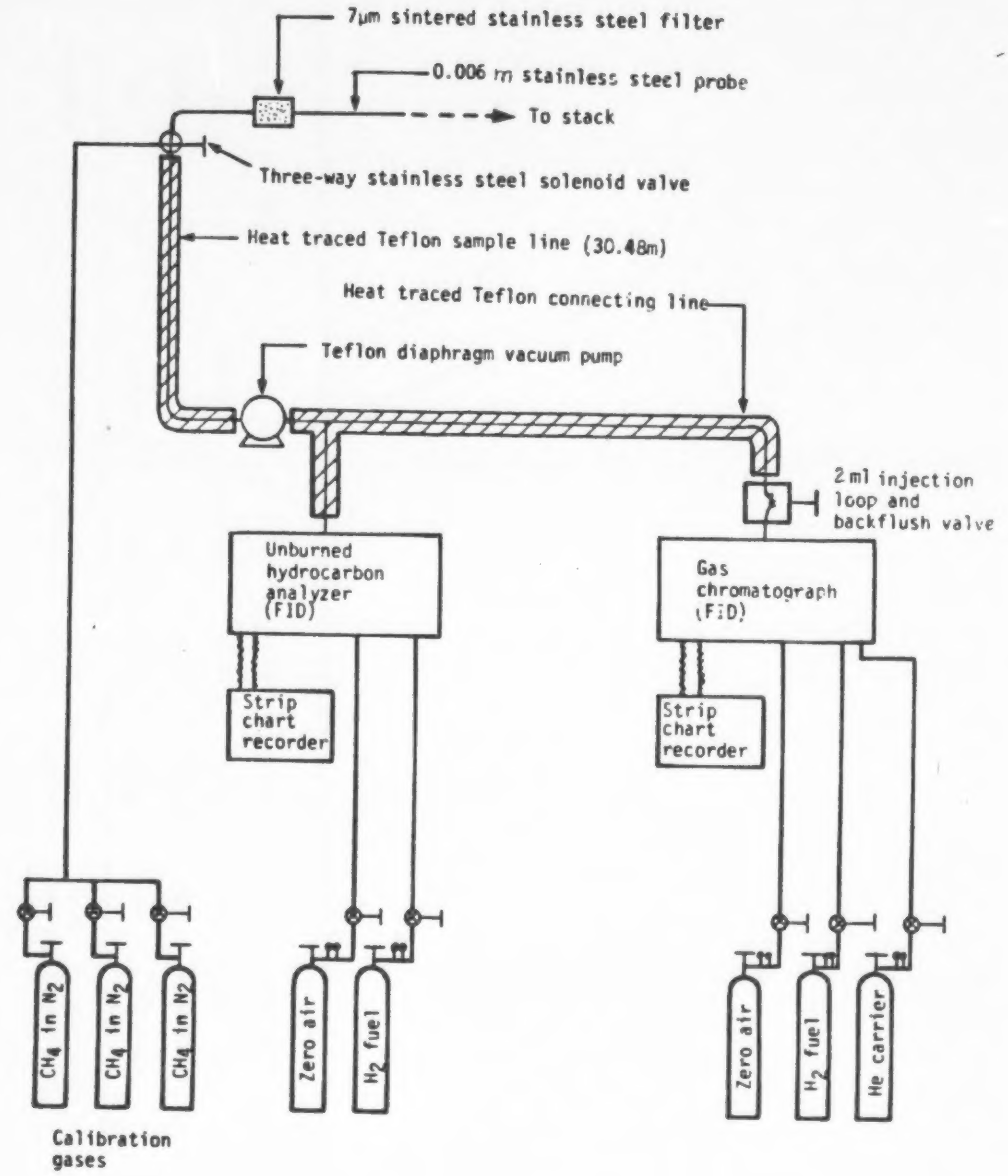

7μm sintered stainless steel filter
0.006 m stainless steel probe
To stack
Three-way stainless steel solenoid valve
Heat traced Teflon sample line (30.48m)
Heat traced Teflon connecting line
Teflon diaphragm vacuum pump
2 ml injection loop and backflush valve
Unburned hydrocarbon analyzer (FID)
Gas chromatograph (FID)
Strip chart recorder
Strip chart recorder
CH_4 in N_2
CH_4 in N_2
CH_4 in N_2
Zero air
H_2 fuel
Zero air
H_2 fuel
He carrier
Calibration gases

Figure C-4. Schematic of unburned hydrocargon and gas chromatograph sampling system.

TABLE C-3. SUMMARY OF ISOKINETIC SOURCE TEST PARAMETERS

Test no.	Date	Test period (24-hr clock)	Sample time (min)	Barometric pressure (inches Hg)	Sample volume (scf)	Average stack gas temp (^0F)	Molecular weight (lb/lb mole dry)	Percent moisture	Percent isokinetic
1	7/22/80	1000-1600	360	30.57	12.79	318.9	29.29	12	98
2	7/23/80	0850-1450	360	30.00	17.34	331.1	29.28	7.2	100.4
3	7/24/80	0850-1450	360	30.69	25.81	342.0	29.43	5.0	100
4	7/25/80	0800-1350	350	30.75	30.64	367.4	29.37	7.9	105.3

Ohio. The filter removed fine particulates which, if allowed to pass into the THC analyzer, could occlude the FID sample inlet capillary. A 0.006m O.D. stainless steel probe connected the filter unit to the heated sampling line via a three-way stainless steel solenoid valve. This valve allowed the introduction of sample gas or calibration gas depending on which mode of operation was desired. A 12.2m, heated-traced, 0.01m O.D. Teflon sample line manufactured by Technical Heaters, Inc. of San Fernando, California, was used to transport the sample to the vacuum pump. Sample line temperature controllers were supplied by the manufacturer. A Teflon-coated diaphragm vacuum pump manufactured by Thomas Industries of Sheboygan, Wisconsin, was used to pull the sample through the lines. From the gas vacuum pump exit, the sample was split and routed to the analyzers via short lengths of heated Teflon line.

Prior to operation and calibration, the completed sampling system was operated at approximately 297°K above normal sampling and calibration conditions, and was purged for several hours with zero nitrogen to remove any traces of residual hydrocarbon contamination in the lines. During this "bake-out" procedure, stainless steel tube unions, filters, and probes were heated using a propane torch. Before and after each test, a leak test was performed on the sampling system, followed by calibration of the THC analyzer using zero nitrogen (<0.5 HC) and a mixture of 535 ppm methane in nitrogen. During calibration, the three-way valve was positioned to block the sample probe and filter, allowing the calibration gas to pass into the heat-traced sample line. Introducing the calibration gases at this location ensured the sample gases and calibrations gases were treated in the same manner, nullifying possible undesirable effects due to absorption or wall loss in the sampling line and system.

C.2.4 Specific Low-Molecular-Weight Hydrocarbon Determination of Flue Gas

Periodically, benzene, toluene, and ethylbenzene concentrations were determined in the boiler flue gas. Small portions of the sampled gas routed to the total hydrocarbon monitoring system was diverted and injected into a Varian Model 3700 gas chromatograph (GC) fitted with an FID. Figure C-4 depicts the sampling system. Using a sample valve fitted with a 2-cm^3 injection loop, the sample was injected into a 6-ft x 1/8-in O.D. stainless steel column packed with 1 percent SP100 on Carbopack (80/100) mesh.

Calibration standards for the compounds of interest were prepared onsite using a 50L Teflon bag and the methods outlined in "Evaluation of Emission Test Methods for Halogenated Hydrocarbons," (Vol. I, EPA-600/4-79-025, March 1979). Table C-4 presents the results of the analysis and a chronology of sampling/injection time during the field testing period.

Resultant chromatographs indicate that the components of interest were not detected at concentrations less than 0.1 ppm in the sampled gas. These data are in close agreement with previously presented data for the total hydrocarbon analysis.

TABLE C-4. SUMMARY OF SPECIFIC LOW MOLECULAR WEIGHT HYDROCARBONS DETERMINATIONS OF FLUE GAS

Date	Time	Procedure	Results*
7-21-80	1623	Injection calibration standards	--
7-22-80	1044	Inject flue gas sample	<0.1 ppm
	1055	Inject flue gas sample	<0.1 ppm
	1110	Inject zero gas	--
	1548	Inject flue gas sample	--
7-23-80	0944	Inject flue gas sample	<0.01 ppm
	1100	Inject flue gas sample	<0.01 ppm
	1304	Inject flue gas sample	<0.01 ppm
	1319	Inject flue gas sample	<0.01 ppm
	1336	Inject calibration standards	--
	1342	Inject flue gas sample	<0.01 ppm
	1349	Inject flue gas sample	<0.01 ppm
	1426	Inject flue gas sample	<0.01 ppm
	1507	Inject flue gas sample	<0.01 ppm
7-24-80	1040	Inject calibration standard	--
	1113	Inject calibration standard	--
	1130	Inject calibration standard	--
	1240	Inject flue gas sample	<0.1 ppm
	1215	Inject zero gas	--
	1400	Inject calibration standard	--
	1415	Inject calibration standard	--
	1430	Inject calibration standard	--
	1449	Inject flue gas sample	<0.01 ppm
7-25-80	0828	Inject calibration standard	--
	0845	Inject calibration standard	--
	0913	Inject flue gas sample	<0.01 ppm
	0940	Inject zero gas	--
	1000	Inject flue gas sample	<0.01 ppm
	1015	Inject C_1-C_6 calibration standard	--
	1125	Inject C_1-C_6 calibration standard	--
	1201	Inject flue gas sample	<0.01 ppm
	1206	Inject flue gas sample	<0.01 ppm

*Concentration of sought components

C.2.5 Composite Sampling

Composite samples of the multicone hopper ash, boiler bottom ash, woodwaste fuel, and sludge/wastewater were collected during the field sampling period. Sampling at these locations was performed at approximate 1-hr intervals during each test run. Samples were obtained by collecting and transferring equal bulk aliquots of the material into precleaned sample storage containers. Figure 7-1 shows the locations of each sampling location.

C.2.6 Grab Sampling

Grab samples of the baghouse hopper ash, pre-processing bulk penta in heavy aromatic treating oil, and bulk creosote were collected during the field sampling. Baghouse No. 2 hopper ash samples were collected at the end of each test run when the hoppers were emptied. Grab samples of the penta and creosote treating formulations were supplied by plant personnel.

C.3 ANALYTICAL METHODS AND RESULTS

Samples from the boiler test site were received on July 29, 1980. The samples were assigned consective laboratory identification numbers and stored at 4°C until analyzed.

C.3.1 Analytical Methods

Analyses were conducted for volatile organics, semivolatile organics and metals. Volatile organics analyses were based on variations to EPA Method 624. Semivolatile organics (phenols and polynuclear aromatics) analyses were based on sample preparation variations to EPA Method 625 in conjunction with fused silica capillary column GC/MS. Metals analyses were conducted using standard atomic absorption techniques.

Analysis of Volatile Organics --

The analytes of interest were benzene, toluene, and ethylbenzene. Only the sludge samples were analyzed for these components.

A 1.0g aliquot of the mixed sludge was weighed into a 15-ml crimp top vial. Pentane (9 ml) and 1-bromo-2-chloropropane (10 μg) were added as internal standards. A 1-μl aliquot of this deluted sample was injected in a 0.2-percent Carbowax 1500 on a Carbopack C packed gas GC in a Finnegan 1020 GC/MS instrument. Analysis and quantitation were conducted per EPA Method 624 using the internal standard method.

Quality control for the volatiles analyses entailed the analyses of a method blank and a method standard spiked at 10 μg/g of sludge.

Analysis of Semivolatile Organics

Semivolatile organics analyzed are listed in Table C-5. These analyses were conducted by variations to EPA Method 625 in the sample preparation and the use of fused silicon capillary column GC/MS to determine these compounds.

TABLE C-5. SEMIVOLATILE ORGANICS ANALYZED IN WOOD PRESERVING SAMPLES

Compound Number	Compound Name
1	Phenol
2	2-Nitrophenol
3	2,4 Dichloropheho1
4	2,4,6 Trichlorophenol
5	4-Nitrophenol
6	4,6-Dinitro-o-cresol
7	Penta
8	Acenaphthene
9	Fluoranthene
10	Napthalene
11	Benz(a)anthracene
12	Chrysene
13	Acenaphthylene
14	Phenanthrene
15	Fluorene
16	Pyrene
17	Anthracene

lower page for EPA format

Sample Preparation --

The sludge samples were prepared as follows:

1. Place 10.0g of the sludge in a clean 250-ml brown bottle. Add 10.0g of anhydrous sodium sulfate and 100 ml of pesticide grade dichloromethane. Shack occassionally and allow to sit overnight at room temperature.

2. Take 1.0 ml of each extract for GC/FID screening. Store the remaining extract at 4°C.

3. As required by the GC/FID screening, filter the extract into a Kuderna-Danish concentrator and concentrate to 1.0 ml.

The GC/FID screening stage was necessary due to the wide variability of sample concentrations. Figure C-5 summarizes the semivolatile extraction scheme for sludge samples.

The XAD-2 cartridge was carefully opened, any silicone stopcock grease removed with a CH_2Cl_2 wetted towel, and the contents transferred to a preextracted Soxhlet thimble. The XAD-2 material in the Soxhlet was spiked with surrogate mix and extracted overnight with CH_2Cl_2. The extract was concentrated to 1 to 100 ml based on the amount of extractable material present.

Quality control for XAD-2 samples consisted of the analysis of surrogate spikes, field blanks and spiked method blanks.

Ash Samples--

20.0g of the flyash were placed in a clean Soxhlet thimble, then spked with surrogates at concentrations of 100 µg. Each sample was extracted with CH_2Cl_2 overnight and concentrated to 1.0 ml. Quality control for ash samples consisted of the use of surrogate spikes and the analysis of a method blank and a spiked sample.

Extract Analysis--

Each of the extracts obtained as described in the previous sections were analyzed for the compounds listed in Table C-5 using fused silica capillary column GC/MS. The instrumental operating conditions are listed in Table C-6.

The quality control requirements listed in EPA Method 625 were followed, including analytical calibration, mass spectrometer tuning to meet decafluorotuphenylphospline (DFTPP) criteria, and the use of the internal standard quantitation method.

Analysis of Metal Species--

Metals were analyzed by standard methods. Sludge samples were vigorously acid-digested prior to analysis for metals using atomic absorption techniques.

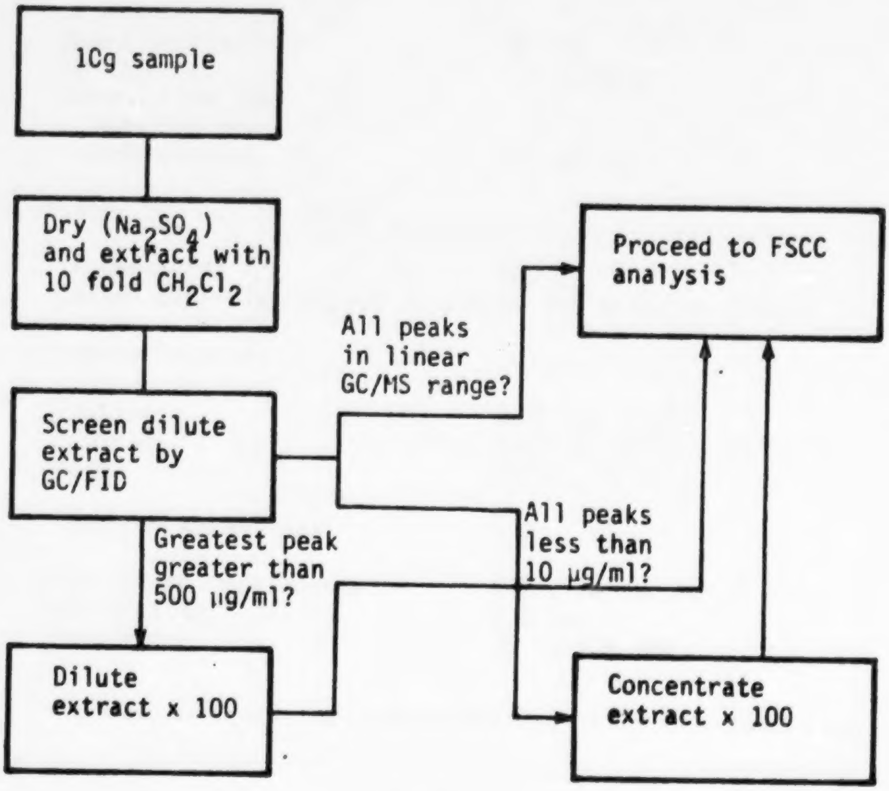

1Cg sample
Dry (Na_2SO_4) and extract with 10 fold CH_2Cl_2
Screen dilute extract by GC/FID
Greatest peak greater than 500 μg/ml?
Dilute extract x 100
All peaks in linear GC/MS range?
Proceed to FSCC analysis
All peaks less than 10 μg/ml?
Concentrate extract x 100

Figure C-5. Analysis scheme for phenols/PAH s in wood preserving sludges.

TABLE C-6. FUSED SILICA CAPILLARY COLUMN PARAMETERS

Column:	
30m x 0.25m SE-54 WCOT (J & W Scientific)	
Splitless Injection Parameters:	
Injection mode:	Splitless
Sweep initiation:	30 sec
Sweep flow:	>12 ml/min
Column flow (He) measured at atmospheric:	1.0 ml/min
Interface:	
Temperature:	300°C
Column directly coupled to source (no transfer lines)	
Temperature Program:	
Initial:	30°C for 2 min
Program:	Ramp to 300°C @ 10°C/min
Hold:	300°C, 15 min
Mass Spectral Parameters:	
Ionization mode/energy:	Electron impact/70 eV
Totoal scan time:	1.0 sec
Mass range:	35 to 475 AMU

C.3.2 Results and Discussion

The quantitative results for the testing during wood and waste incineration are given in Tables C-7 to C-9. Day 1 samples were not analyzed.

Volatile Organics--

Low levels of volatile aromatic hydrocarbons were detected in croesote (Figure C-6). These levels are greatly reduced in the waste sludge. The total hydrocarbon content of the stack gas was 0.01 ppm.

The detected levels of aromatic hydrocarbons in the sludge samples were close to the detection limit. The reported levels have been corrected for method blank contribution. The accuracy of the method at these low nanogram levels is poor. Since the injection of organic extracts on the volatiles GC column led to the accumulation of higher-molecular-weight aromatics. It was necessary to back out the column at 200°C after every few analyses.

Semivolatile Organics

The application of fused silica capillary column GC/MS to this project allowed for greatly improved compound identification over that obtainable with packed column methods. Polynuclear aromatic isomers such as phenanthrene/anthracene and benzo(a)anthracene/chrysene can be resolved by this method. But the Finnegan 4000 capillary injection system is subject to a high degree of front-to-back discrimination. In the split/splitless mode of injection, the sample first is volatilized in the injection port then recondensed at the head of the column. This process results in a substantial variation from injection to injection in the fraction of a given component in the sample placed on the column. An extra degree of random error is introduced into the determination of early eluting compounds (phenol and naphthalene) by decreasing the precision of the analysis. To correct for this effect, the early eluting compound quantitations were corrected using the recovery of the surrogate spike, d_8-naphthalene.

Figure C-7 is a chromatogram from the analysis of semivolatile organics in a sludge sample. The major identified peaks are labelled. There are clearly a large number of organics present in addition to those of interest to this program. Figure C-8 is a chromatogram from a bottom ash extract. Only the polynuclear aromatics were detected in ash samples; no phenols were detected.

Penta and 2-nitrophenol were detected at low but significant levels only in the samples from days 2 and 3. There is no simple explanation of the nitrophenol: this compound was never detected in a sludge or ash sample. Figures C-9 and C-10 are chromatograms of the day 3 XAD-2 cartridge extract and an XAD-2 blank cartridge, respectively. They should be contrasted with C7 and 8.

Metals

The results of the metals analyses are shown in Table C-10.

TABLE C-7. ANALYTICAL RESULTS FOR TEST DAY 2

Compound	Bottom ash*	Baghouse ash*	Mechanical hopper ash*	Sludge*	XAD**
2-Nitrophenol	<0.5	<1.0	<0.5	<10	36
Penta	<0.5	<1.0	<0.5	740	<10
Phenol	<0.1	<0.5	<0.1	1200	2
Fluoranthene	92	0.7	0.5	2200	<1
Naphthalene	10	10	10	1300	280
Benzo(a)anthracene	7.6	<0.5	<0.1	160	<1
Benzo(a)pyrene	1.4	<0.5	<0.1	<20	<5
Benzofluoranthene***	9.3	<0.5	<0.1	52	<5
Chrysene	1.2	<0.5	<0.1	180	<1
Achenaphthylene	4.4	<0.5	<0.1	130	<1
Anthracene	4.5	<0.5	<0.1	760	<1
Benzo(g,h,i)perylene	<0.5	<1.0	<0.5	<20	<5
Fluorene	0.6	<0.5	<0.1	1200	<1
Phenanthrene	24	6.9	0.6	1800	<1
Dibenzo(a,h)anthracene	<0.5	<1.0	<0.5	<20	<5
Indeno(1,2,3-cd)pyrene	<0.5	<1.0	<0.5	<20	<5
Pyrene	29	<0.5	<0.1	1200	<1
Benzene	NA****	NA	NA	1.9	
Toluene	NA	NA	NA	12	
Ethylbenzene	NA	NA	NA	17	

* Concentration in units of μg per gram
** Total μg collected
*** Mixed isomers
**** Not analyzed

TABLE C-8. ANALYTICAL RESULTS FOR TEST DAY 3

Compound	Bottom ash*	Baghouse ash*	Mechanical hopper ash*	Sludge*	XAD**
2-Nitrophenol	<0.5	<1.0	<0.5	<10	74
Penta	<0.5	<1.0	<0.5	260	120
Phenol	<0.8	<0.2	<0.1	1000	<2
Fluoranthene	15	0.2	0.6	340	3
Naphthalene	18	3.9	6.5	1000	1100
Benzo(a)anthracene	0.6	<0.2	<0.1	120	<1
Benzo(a)pyrene	0.1	<0.2	<0.1	<30	<5
Benzofluoranthene***	0.9	<0.2	<0.1	64	<5
Chrysene	0.7	<0.2	<0.1	120	<1
Achenaphthylene	3.0	<0.2	<0.1	68	<1
Anthracene	1.0	<0.2	<0.1	250	<1
Benzo(ghi)perylene	<0.5	<1.0	<0.5	<20	<5
Fluorene	0.8	<0.2	<0.1	420	<1
Phenanthrene	31	3.0	0.5	590	<1
Dibenzo(a,h)anthracene	<0.5	<1.0	<0.5	<20	<5
Indeno(1,2,3-cd)pyrene	<0.5	<1.0	<0.5	<20	<5
Pyrene	7.9	<0.2	<0.1	310	<1
Benzene	NA****	NA	NA	<1.0	NA
Toluene	NA	NA	NA	3.7	NA
Ethylbenzene	NA	NA	NA	5.7	NA

* Concentration in units of µg per gram
** Total µg collected
*** Mixed isomers
**** Not analyzed

TABLE C-9. ANALYTICAL RESULTS FOR TEST DAY 4

Compound	Bottom ash*	Baghouse ash*	Mechanical hopper ash*	Sludge*	XAD**
2-Nitrophenol	<0.5	<1.0	<0.5	<10	<10
Penta	<0.5	<1.0	<7.4	80	<10
Phenol	<0.6	<0.3	<0.1	1400	2
Fluoranthene	1.4	6.2	1.7	170	<1
Naphthalene	9.6	5.1	2.2	560	140
Benzo(a)anthracene	<0.1	<0.5	<0.1	27	<1
Benzo(a)pyrene	<0.1	<0.5	<0.1	<10	<5
Benzofluoranthene***	<0.1	<0.5	<0.1	14	<5
Chrysene	<0.1	<0.5	0.3	28	<1
Achenaphthylene	<0.1	<0.5	<0.1	24	<1
Anthracene	0.2	<0.5	0.2	92	<1
Benzo(ghi)perylene	<0.5	<2.5	<0.5	<20	<5
Fluorene	<0.1	<0.5	<0.1	180	<1
Phenanthrene	3.0	7.3	0.4	330	<1
Dibenzo(a,h)anthracene	<0.5	<2.5	<0.5	<20	<5
Indeno(1,2,3-cd)pyrene	<0.5	<2.5	<0.5	<20	<5
Pyrene	0.4	<0.5	<0.4	140	<1
Benzene	NA****	NA	NA	<1.0	NA
Toluene	NA	NA	NA	9.0	NA
Ethylbenzene	NA	NA	NA	10	NA

* Concentration in units of μg per gram
** Total μg collected
*** Mixed isomers
**** Not analyzed

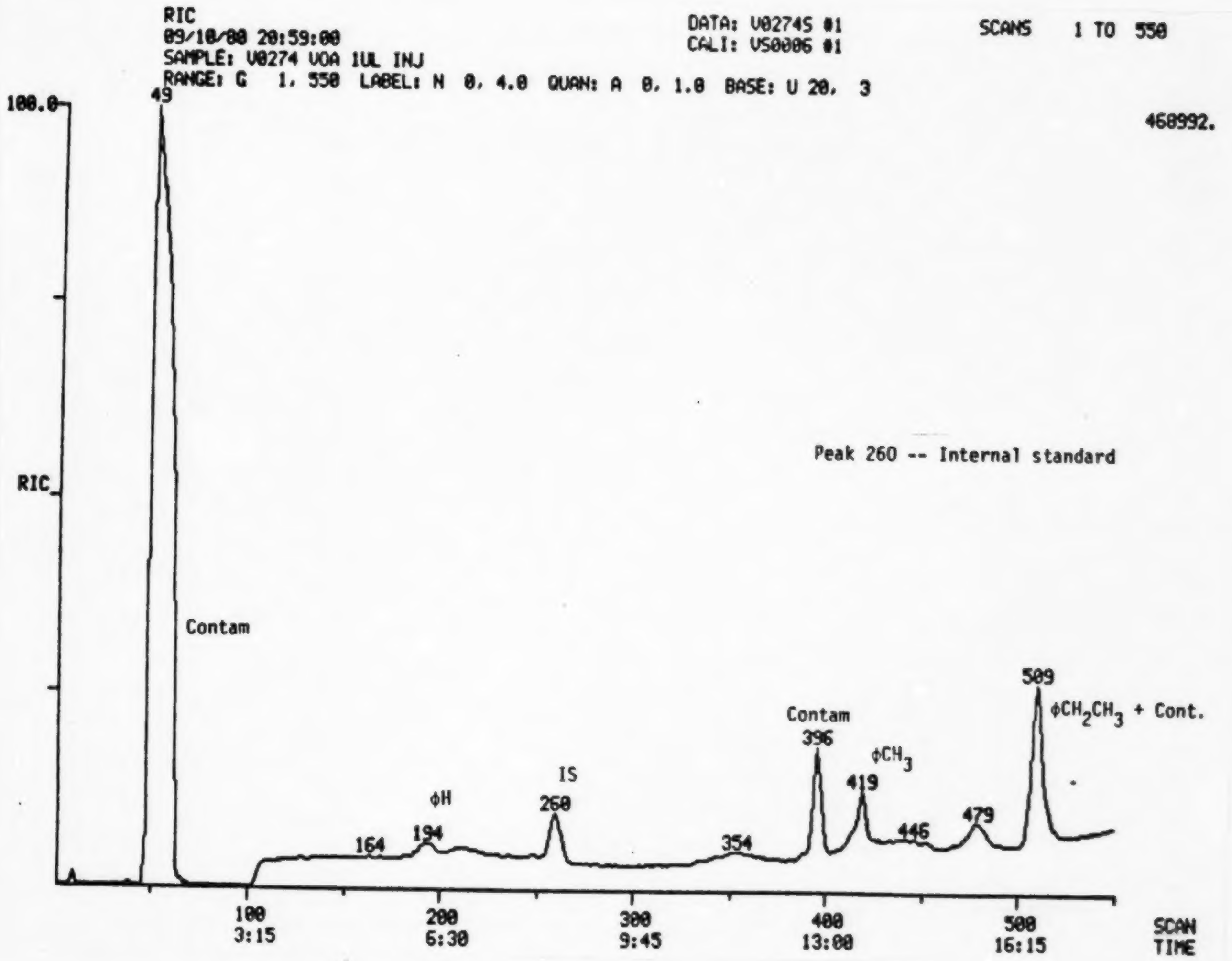
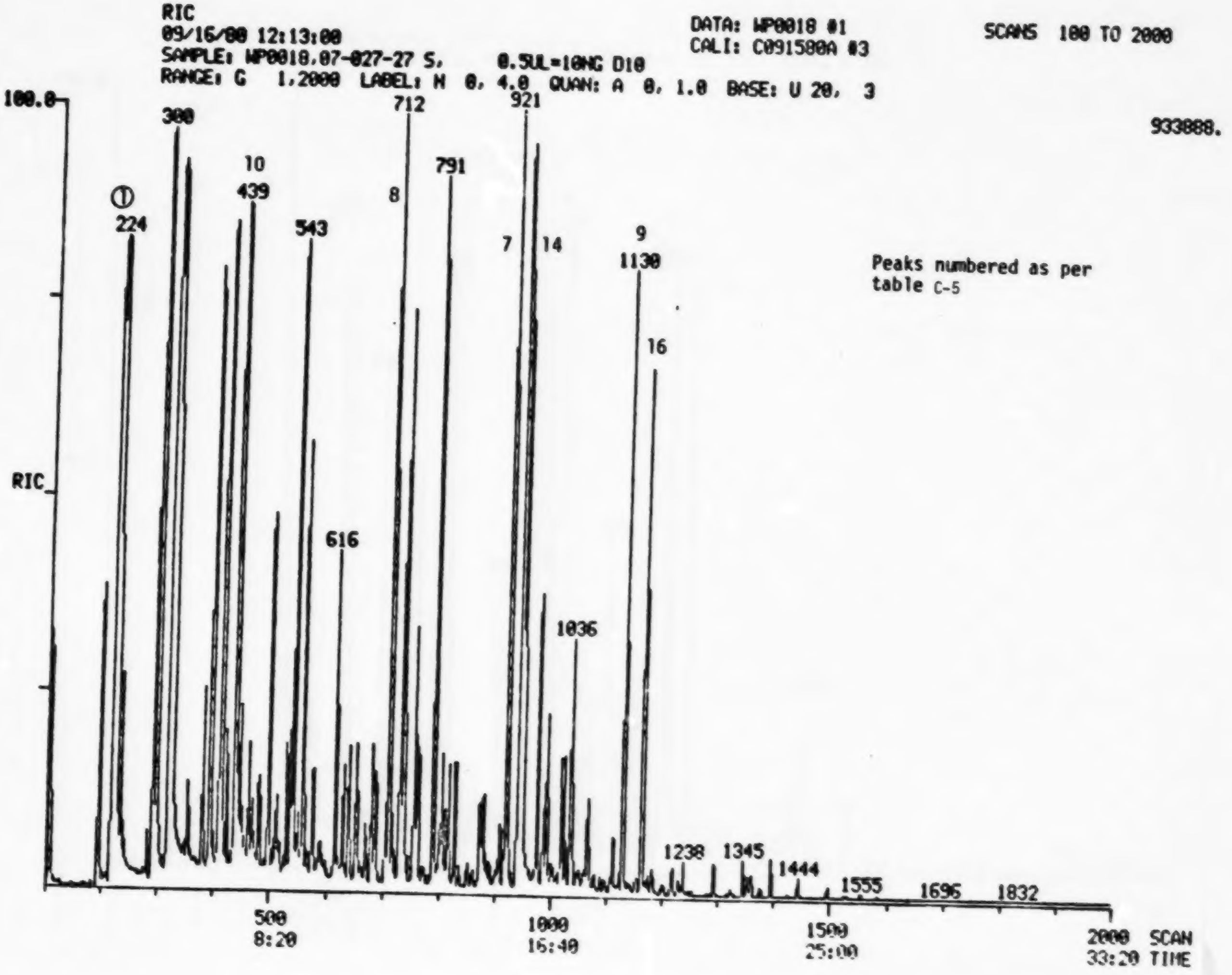


Figure C-6. Volatiles analysis of diluted creosote.



Peaks numbered as per table C-5

Figure C-7. Total ion current chromatogram of waste sludge extract.

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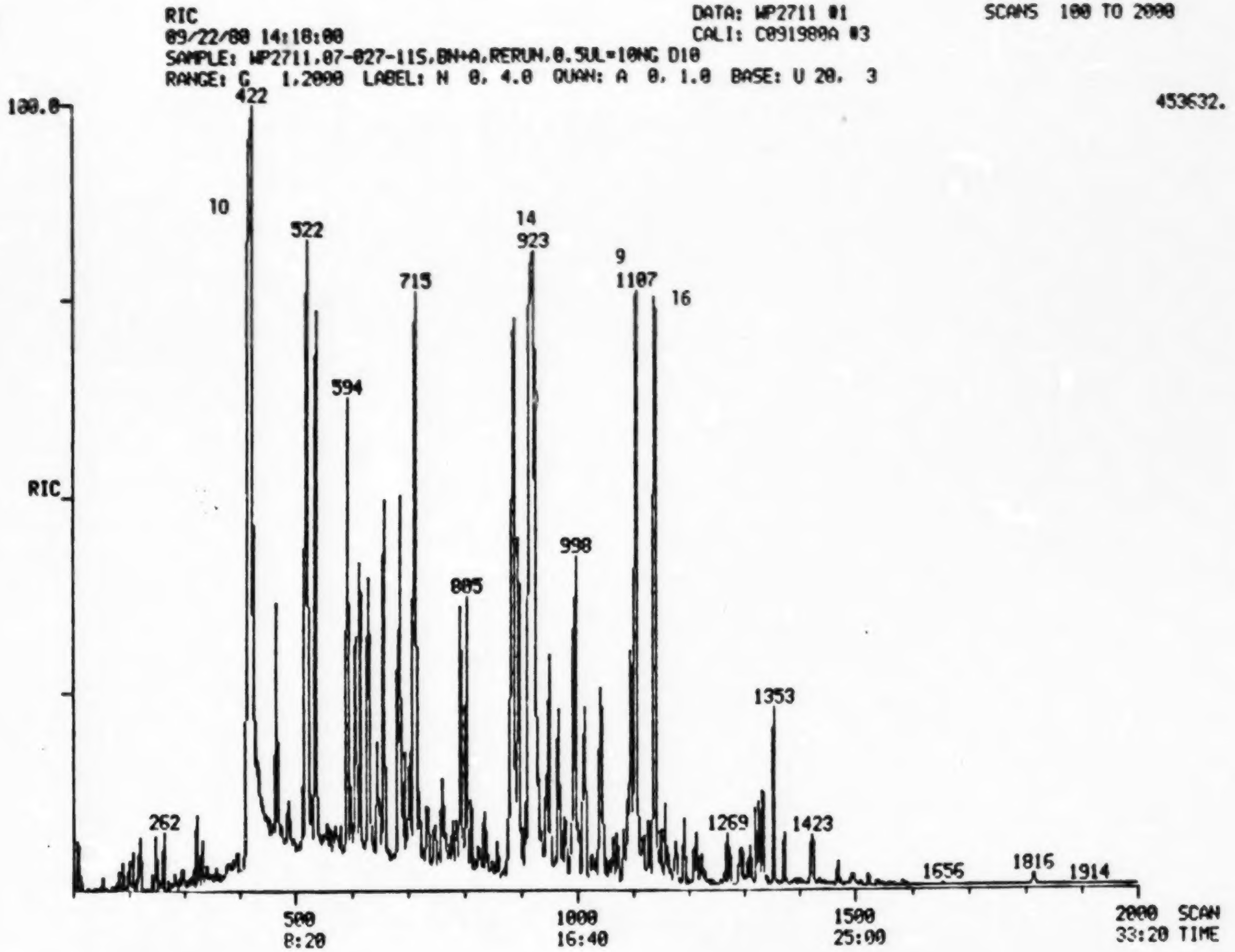


Figure C-8. Total ion current chromatogram of bottom ash extract.

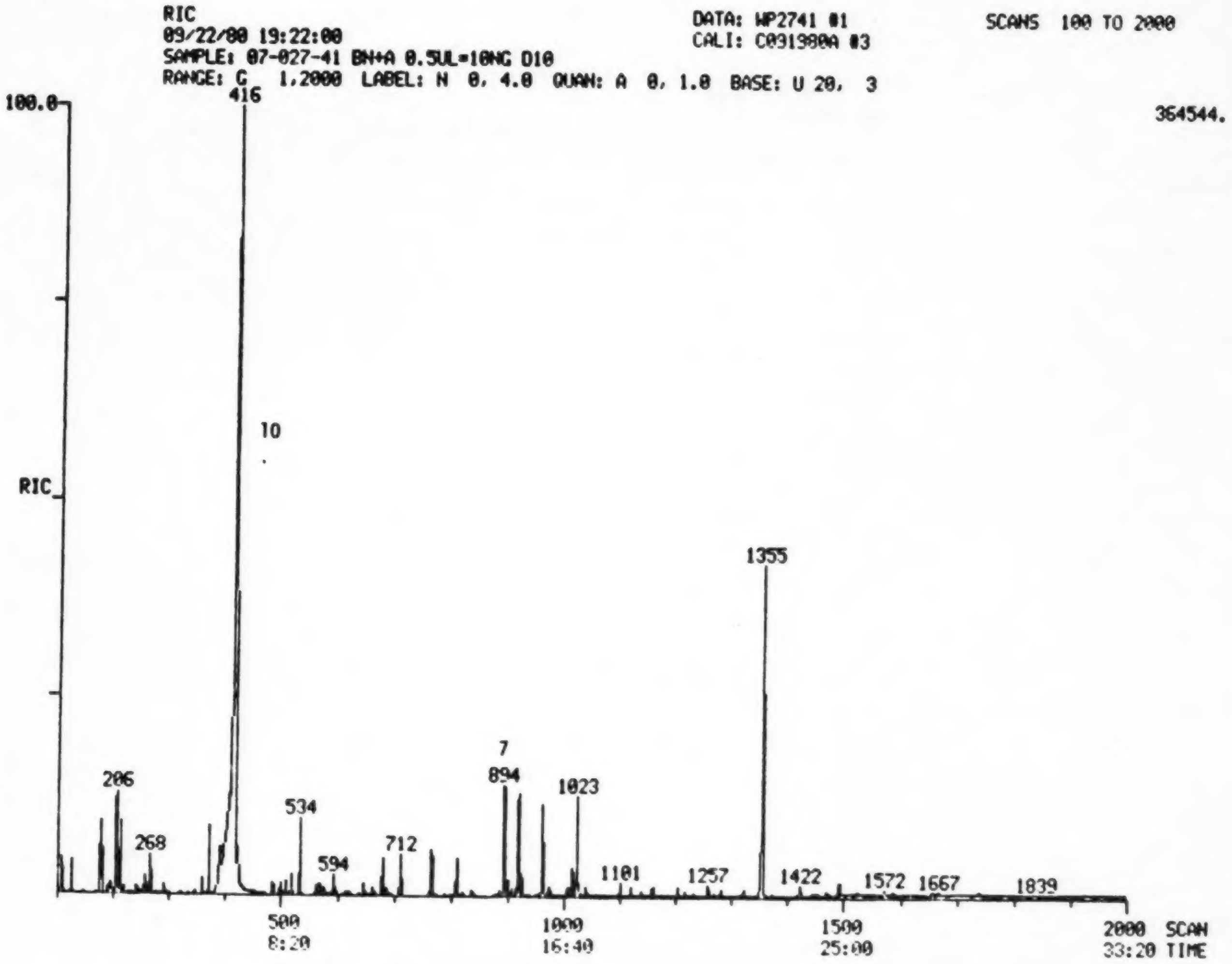


Figure C-9. Total ion current chromatogram of an XAD-2 extract.

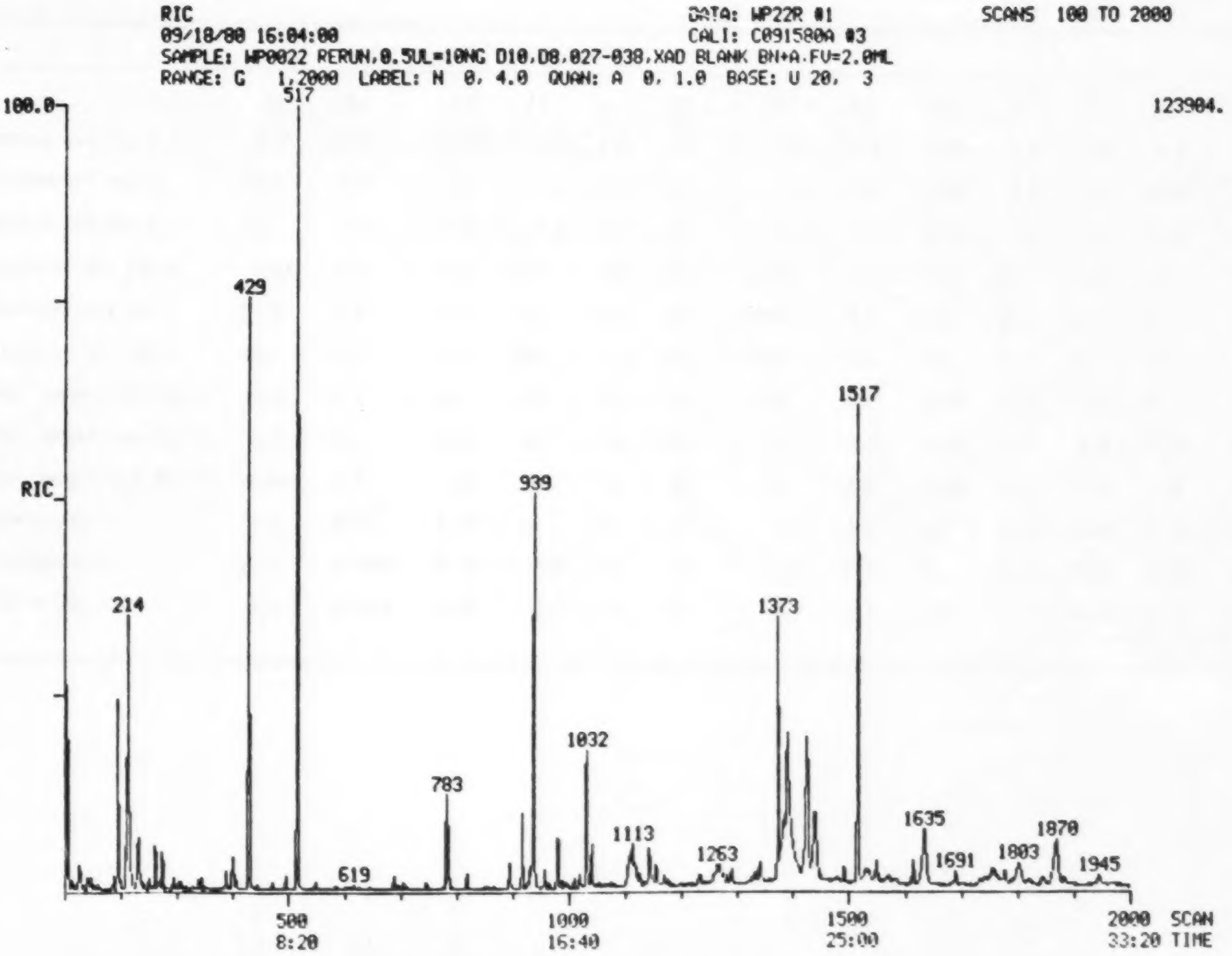


Figure C-10. Total ion current chromatogram from an XAD-2 blank cartridge.

TABLE C-10. METALS ANALYSIS

	ppm												
	As	Be	Cd	Zn	Cr	Cu	Pb	Ni	Ag	Sb	Hg	Se	Ti
Bottom ash day 2	0.35	1.0	0.02	2.0	1.0	29	1.0	0.6	0.06	5.0	1.0	5.0	0.1
Bottom ash day 3	40.5	0.7	0.02	5.0	0.6	57	1.0	0.5	0.06	5.0	2.0	10.0	0.1
Bottom ash day 4	73	1.0	0.02	8.0	1.1	29	1.0	0.4	0.06	5.0	0.9	10.0	0.1
Baghouse ash day 2	0.53	0.4	0.3	750	2.9	230	1500	0.4	0.1	25	5.0	5	0.1
Baghouse ash day 3	11.4	0.4	0.4	750	4.4	305	1500	0.4	0.1	38	12	10	0.1
Baghouse ash day 4	49	0.2	0.3	500	3.4	225	1200	0.2	0.1	28	11	10	0.1
Med. hopper ash day 2	0.02	2.0	0.1	90.	1.9	85	100	0.3	0.06	5.0	3.0	10	0.1
Med. hopper ash day 3	6.5	0.9	0.02	40	2.0	120	10	0.3	0.06	5.0	4.0	5.0	0.1
Med. hopper ash day 4	0.88	0.9	0.02	30	1.8	70	10	0.2	0.06	5.0	2.0	5.0	0.1
Sludge day 2	6.8	0.001	0.02	1C	2.7	36	1.0	0.2	0.06	0.05	0.01	0.05	0.001
Sludge day 3	3.5	0.0009	0.02	7.0	2.6	48	1.0	0.2	0.06	0.25	0.01	0.05	0.001
Sludge day 4	8.1	0.0009	0.02	3.0	2.0	19	1.0	0.2	0.06	0.16	0.02	0.10	0.001

4

C.4 LABORATORY A ANALYTICAL RESULTS

C.4.1 Analytical Methodology

A. Extraction and Cleanup Procedures

The seven samples received for analysis include three different sample types. Sludge and Penta in Oil may be treated as one type of sample, ash is a second type, and the blank is a third sample type. Each of these types of samples required different procedures for extracting the CDDs and CDFs. However, the subsequent steps involved in cleanup of the sample extracts, as well as the mass spectrometric procedures employed to quantitate the compounds of interest were common to all samples. The three sample extraction methods are outlined below, followed by a description of the methods common to all samples.

1. Sludge and Penta in Oil Samples

a. Place an accurately weighed aliquot (typically 1g) of the sample in a clean flint glass bottle (Teflon-lined screw cap). Add the internal standard solution (225 μl of benzene containing 25 ng $^{37}Cl_4$-2,3,7,8-TCDD and 200 ng $^{37}Cl_4$-1,2,3,4,6,7,8-HpCDD) add 40 ml of hexane, and agitate to dissolve the sample.

Proceed as outlined in the steps common to all samples listed below.

2. Ash Samples

a. Place an accurately weighed aliquot (typically 1g) of the ash into a glass extraction thimble, add the internal standard solution (225 μl benzene containing 25 ng $^{37}Cl_4$-2,3,7,8-TCDD and 200 ng $^{37}Cl_4$-1,2,3,4,6,7,8-HpCDD) to the sample, and place the thimble in a Soxhlet extractor.

b. Extract the sample for 16 hours using benzene as the extraction solvent.

c. Concentrate the extract to about 0.5 ml in a stream of prepurified nitrogen while heating the sample at 55° in a water bath.

d. Quantitatively transfer (using hexane as the transfer solvent) the concentrate to a clean 125 ml flint glass bottle (Teflon-lined screw cap), and add additional hexane, so that a total of 40 ml hexane is present in the bottle.

Proceed with the steps common to all samples listed below.

3. Blank Sample

a. Place the internal standard solution into the bottle (225 μl of benzene containing 25 ng $^{37}Cl_4$-2,3,7,8-TCDD and 200 ng $^{37}Cl_4$-1,2,3,4,6,7,8-HpCDD).

b. Add about 200 ml of hexane to the bottle and agitate for 5 minutes. Quantitatively transfer the hexane extract to a clean 125 ml flint glass bottle (Teflon-lined screw cap) and rinse the blank bottle with sufficient hexane to obtain a final volume of 40 ml of hexane and combine all hexane extracts in the 125 ml flint glass bottle.

Proceed as outlined in the steps common to all samples listed below.

4. Cleanup Procedures Applied to all Samples

a. Extract the organic solution with 50 ml of 20 percent (w/v) potassium hydroxide by agitating for 10 minutes. Allow for complete separation of aqueous and organic layers and remove aqueous base (bottom) layer to base waste bottle.

b. Extract the organic solution with 50 ml of doubly distilled water by agitating the sample for 2 minutes. Allow time for complete layer separation and discard the aqueous (bottom) layer.

c. Extract the organic solution with 50 ml of concentrated sulfuric acid (cautiously adding sulfuric acid) by agitating the sample for 15 minutes. Allow for complete layer separation and discard acid (bottom) layer into acid waste bottle.

d. Repeat Step 3 until acid layer is nearly transparent.

e. Extract the organic solution with 50 ml of doubly distilled water by agitating for 2 minutes. Allow for complete separation and remove aqueous (bottom) layer.

f. Dry the organic layer over sodium sulfate and then quantitatively transfer a portion of the organic layer to a clean test tube and reduce the volume to incipient dryness using a stream of prepurified nitrogen and while maintaining the test tube in a 55° water bath.

g. Fabricate a glass Macro-column (20 mm OD x 230 mm long) tapered to 6 mm OD on one end. Pack the column with 1.0 g silica, 2.0 g silica containing 33 percent (w/w) IM NaOH, 1.0 g silica, 4.0 g silica containing 44 percent (w/w) concentrated, sulfuric acid and 2.0 g silica. Quantitatively transfer the residue obtained in Step f to the column with 45 ml hexane. Collect the eluent and concentrate to 1 to 2 ml in a centrifuge tube.

h. Construct a disposable liquid chromatography column as follows. Cut off a Pyrex 5 ml disposable pipet at the 2 ml mark and use the lower portion of the pipet. Pack the samll end with a plug of silanized glass wool. Next add 1 gram of Woelm basic alumina previously activated overnight at 600°C in a muffle furnace and placed in a dessicator for 30 minutes just prior to use.

i. Using a disposable pipet, transfer the sample onto the liquid chromatography column.

j. Rinse the centrifuge tube with 2 consecutive 0.3 ml portions of 3 percent CH_2Cl_2 in hexane, and transfer the rinses to the alumina column.

k. Elute the column with 10 ml of 3 percent (v/v) CH_2Cl_2 in hexane and discard the eluent (taking care not to let the column run dry).

l. Elute the column with 15 ml of 50 percent (v/v) CH_2Cl_2 in hexane and retain the eluent for analysis.

m. Concentrate the solution to approximately 1 ml, using a stream of prepurified nitrogen as before. Rinse the centrifuge tube wall with an additional 1 ml of CH_2Cl_2 and reconcentrate.

n. Quantitatively transfer the residue (using methylene chloride) to two 2 ml micro-reaction vessels (one-half of the residue in each vessel). The contents of one vessel are used for CDF determinations and the contents of the other vessel for CDDs.

o. Evaporate the solution in each of the micro-reaction vessel almost to dryness as previously, rinse the walls of each vessel with approximately 0.5 ml CH_2Cl_2, and evaporate contents just to dryness.

p. Approximately 1 hour before GC/MS (GC/LRMS or GC/HRMS) analysis, dilute the residue in the micro-reaction vessel with benzene to the required amount. Gently swirl benzene on portion of vessel to ensure dissolution of the dioxins.

q. If upon preliminary GC/MS analysis the sample appears to contain interferences, high performance liquid chromatographic clean-up of the extract is accomplished at this point prior to further GC/MS analysis. For HPLC, a Varian Model 5021 instrument is employed equipped with a DuPont Zorbax-ODS (C-18, reverse phase) column. See below for further HPLC details.

B. Gas Chromatography/Mass Spectrometry Procedures

a. Parameters for Gas Chromatographic-High Resolution Mass Spectrometric (GC-HRMS) Analysis of the Extracts.

Instrumentation: Varian 3740 Gas Chromatograph coupled through an AEI silicone membrane separator to a modified AEI MS-30 Mass Spectrometer. Modifications to the MS-30 include changes in the ESA power supply to permit inclusion of a custom built, step-scan circuit which is driven by a Nicolet 1074 Signal Averaging Computer. Four masses are rapidly scanned at the retention time of the dioxin or furan of interest.

Conditions for the Gas Chromatograph:

Column: 1.8m x 2mm I.D. glass column packed with 1.5 percent OV-101 on Gas Chrom Q (100/120 mesh)

Carrier Gas: Helium at a flowrate of 30 ml/min

Temperature:
Injector: 250°C
Column: 220°C
Transfer Lines: 285°C

Conditions for the Mass Spectrometer:

Ionizing Voltage: 70 eV
Static Resolution: 1:12,500 (10 percent Valley)
Source Envelope Pressure: 5×10^{-5} torr
Analyzer Pressure: 5×10^{-5} torr
Source Temperature: 250°C
Membrane Separator Temperature: 215°C

Transfer Line: 270°C

Masses Monitored: m/z 319.8966, 321.8936, 325.8805, 327.8846

b. Parameters for Gas Chromatographic-Low Resolution Mass Spectrometric (GC-LRMS) Analysis of the extracts:

Instrumentation: Perkin-Elmer Sigma II Gas Chromatograph coupled through a custom-fabricated interface including a single-stage glass jet separator to a Kratos MS-25 Mass Spectrometer equipped with a DS-50SM Data System.

Conditions for the Gas Chromatograph:

Column: 50M WCOT (OV-101) Silica Capillary

Carrier Gas: Hydrogen, 30 lb. head pressure

Column Temperature: Programmed from 190°C to 220°C σ 5°C/min, hold at 220°C for 20 min.

Interface Temperature: 250°C

Injector: Split ratio 50:1

Conditions for the Mass Spectrometer:

Selected Ion Monitoring Mode (for m/z's monitored and details of instrumental procedures see Tables C-11, C-13)

Ionizing Voltage: 70 eV

Accelerating Voltage: 4 KV

C. High Performance Liquid Chromatography Procedures

a. Parameters for high performance liquid chromatographic (HPLC) clean-up of the extracts:

Instrumentation: Varian Model 5021 Microprocessor Controlled High Performance Chromatograph equipped with CDS-111L Data System

Parameters:

Pressure: Minimum: 10 atm
Maximum: 250 atm

Injection Loop: 25 µl

Column: Guard: 35 µ Vydac SC Reverse Phase
4.0 cm x 0.4 cm I.D.

Analytical: 2-DuPont Zorbax-ODS
25.0 cm x 0.6 cm I.D.

Temperature: Guard Column: Ambient
Analytical Column: 50^{o}C

Detector: Fixed UV: 254 nm, 0.01 A.U.F.S.

Variachrom UV-Vis: TCDD, 235 nm, 0.01 A.U.F.S.
HxCDD, HpCDD, 245 nm, 0.01 A.U.F.S.

Program:

Time	Code	Value
.0	Δ	100 Methanol
.0	Flow	2.5 ml/min
.0	Event	Hold
.1	Event	Inject
20.0	Event	Reset

TABLE C-11. LIST OF ION MASSES MONITORED USING GC-SELECTED-ION MONITORING MASS SPECTROMETRY FOR SIMULTANEOUS DETERMINATION OF MONO-, DI-, TRI-, TETRA-, PENTA-, HEXA-, HEPTA-, AND OCTA-CHLORINATED DIBENZO-p-DIOXINS AND DIBENZOFURANS

Class of Chlorinated Dibenzodioxin or Dibenzofuran	Number of Chlorine Substituents (X)	Monitored m/z for Dibenzofurans $C_{12}H_{8-x}OCl_x$	Monitored m/z for Dibenzo-p-dioxins $C_{12}H_{8-x}O_2Cl_x$	Approximate Theoretical Ratio Expected on Basis of Isotopic Abundance
Mono-	1	202.019[a] 204.016	218.013[a] 220.011	1.00 0.35
Di-	2	235.980[a] 237.977	251.974[a] 253.972	1.00 0.69
Tri-	3	269.941[a] 271.938	285.940[a] 287.937	0.99 1.00
Tetra-	4	303.902[a] 305.899	319.897[a] 321.894 327.885[b] [256.933 258.930][c]	0.74 1.00 — 0.21 0.20
Penta-	5	337.863[a] 339.860	353.858[a] 355.855	0.57 1.00
Hexa-	6	373.821 375.818	389.816 391.813	1.00 0.87
Hepta-	7	407.782 409.779	423.777 425.774 431.765[b]	1.00 1.00 —
Octa-	8	441.743 443.740	457.738 459.735	0.86 1.00

[a] Molecular ion peak.

[b] $^{37}Cl_4$-labelled HpCDD standard peak.

[c] Ions which can be monitored in TCDD analyses for confirmation purposes.

TABLE C-12. SEQUENCE OF OPERATIONS IN GC/MS (MS-25) ANALYSES OF CHLORODIBENZODIOXINS AND CHLORODIBENZOFURANS IN FIRST INJECTION OF SAMPLE EXTRACT

ELAPSED TIME (MIN)	EVENT	GC COLUMN TEMPERATURE	TEMPERATURE PROGRAM RATE (Δ°C/MIN)	IONS MONITORED BY MASS SPECTROMETER (m/z)	COMPOUNDS MONITORED
0.00	Injection, splitless	190°C	—		
1.50	Turn on split valve	190°C	—		
2.00	Begin temp program to 220°C	190°C	5°C/min		
4.50	Open column flow to Mass Spec.	202°C	5°C/min		
5.00	Start PROGRAM #1				
	Sweep = 100 ppm				
	Time on each mass = 0.15 sec	205°C	5°C/min	202.019	Mono-Cl furans
				204.016	Mono-Cl furans
				218.013	Mono-Cl dioxins
				220.011	Mono-Cl dioxins
8.00	Column reaches isothermal hold	220°C	—		
8.75	Stop PROGRAM #1	220°C	—		
9.50	Start PROGRAM #3				
	Sweep = 100 ppm				
	Time on each mass = 0.15 sec	220°C	—	269.941	Cl_3 furans
				271.938	Cl_3 furans
				285.940	Cl_3 dioxins
				289.937	Cl_3 dioxins
16.00	Stop PROGRAM #3				
16.75	Start PROGRAM #5	220°C	—		
	Sweep = 125 ppm			327.885	^{37}Cl labelled TCDD
	Time on penta mass = 0.2 sec			337.863	Cl_5 furans
	Time on ^{37}Cl-TCDD = 0.07 sec			339.860	Cl_5 furans
				353.858	Cl_5 dioxins
				355.855	Cl_5 dioxins
25.00	Begin temp program to 235°C	220°C	5°C/sec		
28.00	Stop PROGRAM #5	235°C			
45.00	Start PROGRAM #7				
	Sweep = 175 ppm				
	Time on each mass = 0.35 sec	235°C	—	407.782	Cl_7 furans
				409.779	Cl_7 furans
				423.777	Cl_7 dioxins
				425.774	Cl_7 dioxins
				431.765	^{37}Cl labelled HpCDD
60.00	Stop PROGRAM #7				
95.00	Return GC to initial temp				

TABLE C-13. SEQUENCE OF OPERATIONS IN GC/MS (MS-25) ANALYSES OF CHLORODIBENZODIOXINS AND CHLORODIBENZOFURANS IN SECOND INJECTION OF SAMPLE EXTRACT

ELAPSED TIME (MIN)	EVENT	GC COLUMN TEMPERATURE	TEMPERATURE PROGRAM RATE (Δ°C/MIN)	IONS MONITORED BY MASS SPECTROMETER (m/z)	COMPOUNDS MONITORED
0.00	Injection, splitless	190°C	—		
1.50	Turn on split valve	190°C	—		
2.00	Begin temp program to 220°C	190°C	--		
4.50	Open flow to Mass Spec.	202°C	5°C/min		
6.00	Start PROGRAM #2	210°C	5°C/min	235.980	Cl_2 furans
	Sweep = 100 ppm			237.977	Cl_2 furans
	Time on each mass = 0.15 sec			251.974	Cl_2 dioxins
				253.972	Cl_2 dioxins
8.00	Column reaches 220°C	220°C	—		
	hold isothermal				
12.00	Stop PROGRAM #2	220°C	—		
12.75	Start PROGRAM #4	220°C	—	303.902	Cl_4 furans
	Sweep = 100 ppm			305.899	Cl_4 furans
	Time on CL_4 mass = 0.15 sec			319.897	Cl_4 dioxins
	Time on ^{37}Cl-TCDD = .05 sec			321.894	Cl_4 dioxins
				327.885	^{37}Cl labelled TCDD
24.00	Stop PROGRAM #4	220°C	--		
25.00	Begin temp program to 235°C	220°C	5°C/min		
26.00	Start PROGRAM #6	225°C	5°C/min	373.821	Cl_6 furans
	Sweep = 150 ppm			375.818	Cl_6 furans
	Time on each mass = .25 sec			389.816	Cl_6 dioxins
				391.813	Cl_6 dioxins
45.00	Stop PROGRAM #6	235°C	--		
46.00	Start PROGRAM #7	235°C	—	407.782	Cl_7 furans
	Sweep = 175 ppm			409.779	Cl_7 furans
	Time on each mass = .035 sec			423.777	Cl_7 dioxins
				425.774	Cl_7 dioxins
				431 765	^{37}Cl labelled TCDD
60.00	Stop PROGRAM #7	235°C	--	441.743	Cl_8 furans
70.00	Start PROGRAM #8	235°C	--	443.740	Cl_8 furans
	Sweep = 225 ppm			457.738	Cl_8 dioxins
	Time on each mass = 0.55 sec			459.735	Cl_8 dioxins
90.00	Stop PROGRAM #8	235°C			
95.00	Return to initial temp				

C.4.2 Results and Discussion

As indicated in the procedural GC/MS discussion presented in the previous pages, two separate gas chromatographic-mass spectrometric methods of analysis were employed in this program, one utilizing low resolution gas chromatography-high resolution mass spectrometry (LRGC-HRMS), and the other utilizing high resolution gas chromatography-low resolution mass spectrometry (HRGC-LRMS). For determination of total TCDDs in the extracts of the samples LRGC-HRMS was employed. This technique yields essentially unequivocal quantitative results for the total TCDDs present in the analyte, but does not yield information regarding the specific TCDD isomers which are present. The results obtained with this method for the samples are listed in Table C-14. Both m/z 320 and m/z 322 (these are nominal masses, actual m/z's monitored were 319.8966 and 321.8936) were monitored as indicators of TCDD during the period when TCDDs elute from the gas chromatograph and thus, quantitation of the TCDDs detected can be based upon the signal observed at either mass. The theoretical ratio of m/z 320:m/z 322 resulting from TCDD (based on the known isotropic abundances of ^{35}Cl and ^{37}Cl and the numbers of Cl substituents in the molecular ion) is 0.77, and as can be seen from the data, since the TCDD values calculated from the response at each ion mass are reasonably consistent, the experimentally observed ratio is essentially the same as the theoretical ratio. This is another criterion which the data should satisfy in order to certify with confidence that TCDD is indeed detected. Since the mass at m/z 327.8846, which arises from the $^{37}Cl_4$-2,3,7,8-TCDD internal standard added to all samples prior to processing, was monitored concurrently with the two masses typical of native TCDDs, and the quantitation of native TCDDs is actually based upon the ratios of the signals at m/z 320 and m/z 322 to that at m/z 328, the values listed in Table C-14 are inherently "recovery corrected." This is, of course, one of the chief reasons for utilizing an internal standard, and results in improved accuracy. The percent recovery of the internal standard is listed solely for the purpose of illustrating the overall efficiency of the analytical procedure. Clearly, the recoveries are generally quite high and the procedures are, therefore, acceptable for analyses of these samples.

For determining the concentrations of each of the various classes (monochlorinated through octachlorinated) of chlorinated dibenzo-p-dioxins and dibenzofurans in the sample extracts a sophisticated HRGC-LRMS technique was employed. As indicated in the previous section, a complex computer-controlled multiple ion monitoring scheme was employed. The compounds in each extract were quantitated during two separate GC/MS analyses. The chromatographic and mass spectrometric conditions employed and the ions monitored during the two GC/MS analyses were given previously in Tables C-12 and 13. These conditions permit m/z's typical of each class of the CDDs and CDFs to be monitored during the appropriate time interval corresponding to the gas chromatographic retention time interval for the various members of a given class. As expected, the monochlorinated CDDs and monochlorinated CDFs have similar retention times. However, use of the 50 M (WCOT) fused silica column provides optimum separation and minimized overlap of individual compounds. It must be noted that of the 75 possible CDDs and 135 possible CDFs, authentic standards of only a limited number were available for use in calibration. Most of the

TABLE C-14. LOW RESOLUTION GAS CHROMATOGRAPHIC-HIGH RESOLUTION MASS SPECTROMETRIC ANALYTICAL RESULTS FOR ACUREX SAMPLES

		TOTAL TCDD DETECTED				
WSU SAMPLE NO.	**ACUREX SAMPLE NO.**	**m/z 320**	**m/z 322**	**AVERAGE**	**M.D.C. ng/g**	**PERCENT RECOVERY**[a]
ACC-11	80-07-027-3	1.1 ppb	1.10 ppb	1.11 ppb	0.5	121
ACC-12	80-07-027-26	0	0	0	0.2	108
ACC-13	80-07-027-26(28)	0	0	0	0.9	24
ACC-14	80-07-027-43	3.7 ppb	3.4 ppb	3.4 ppb	0.2	126
ACC-15	80-07-027-44	0.9 ppb	0.8 ppb	0.8 ppb	0.2	85
ACC-16	80-07-027-44(45)	3.3 ppb	3.3 ppb	3.3 ppb	0.2	135
ACC-17	Blank, Empty Bottle	0	0	0	0.3	93

[a] Based on $^{37}Cl_4$-2,3,7,8-TCDD added as an internal standard prior to sample processing.

CDD and CDF peaks observed in the analyses of the sample extracts cannot be assigned to a specific isomer. Thus, in arriving at a quantitative value for a given class of CDDs or CDFs, the areas of the mass chromatographic peaks appearing at the appropriate retention times, and having the appropriate mass spectral response, were summed and compared to the corresponding area observed from injection of a known quantity of a calibration standard of the same class. In general, a single CDD or CDF isomer of each chlorinated group (i.e., monochlorinated, dichlorinated, etc.) was used in the calibration process. Mass chromatograms were obtained in the course of the complete GC-MS scans resulting from two injections of a mixture of such CDD and CDF standards. The CDD and CDF isomers used in obtaining this calibration data were 1-chlorodibenzo-p-dioxin; 2,7-dichlorodibenzo-p-dioxin; 1,2,4-trichlorodibenzo-p-dioxin; 2,3,7,8-tetrachlorodibenzo-p-dioxin; $^{37}Cl_4$-2,3,7,8-tetrachlorodibenzo-p-dioxin; 1,2,3,4,7,8-hexachlorodibenzo-p-dioxin; 1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin; octachlorodibenzo-p-dioxin; 2,4-dichlorodibenzofuran; 1,2,4-trichlorodibenzofuran; 2,3,7,8-pentachlorodibenzofuran; 1,2,4,5,6,7,9-hexachlorodibenzofuran; and octachlorodibenzofuran.

Mass chromatograms resulting from the full GC/MS scan of two injections of Acurex Sample 80-07-027-43 for all classes of CDDs and CDFs are shown in Figures C-11 through 28. The concentrations of CDDs and CDFs in all the Acurex samples analyzed, determined from similar GC/MS data, are presented in Section 8.

In the case of the TCDDs, the HRGC-LRMS system was employed to partially elucidate the identity of the specific TCDD isomers present in each of the sample extracts orginally found by LRGC-HRMS to contain TCDDs. Figure C-28 shows the mass chromatograms resulting from injection of a calibration standard containing 12 separate TCDD isomers, as well as the $^{37}Cl_4$-2,3,7,8-TCDD internal standard. Figure C-28 shows the result of analyzing another calibration mixture containing only 5 isomers and the $^{37}Cl_4$-2,3,7,8-TCDD internal standard. Finally in Figures C-29 and 30 HRGC-LRMS results for two of the Acurex samples are shown. As can be seen in Figure C-30 this sample extract apparently contains 4 TCDD isomers (as well as the $^{37}Cl_4$-2,3,7,8-TCDD internal standard). However, some of these peaks may be representative of more than one isomer. In fact, some of these peaks are rather broad, suggesting that other isomers may indeed be present. Noteworthy is the fact that the 2,3,7,8-isomer is clearly absent in this sample extract. Finally, as shown in Figure C-30, five or possibly six TCDD isomers are apparently present in sample α80-07-027-44(45). Here again some of the discrete peaks may represent multiple isomers. The results displayed in Figure 4 suggest that only a trace of the 2,3,7,8-TCDD isomer may be present in this sample. A summary list of standards used by this laboratory is given in Table C-15.

C.5 LABORATORY B ANALYSIS

Laboratory B received five samples for CDD and CDF analysis. As these samples required extensive cleanup procedures, they are listed separately.

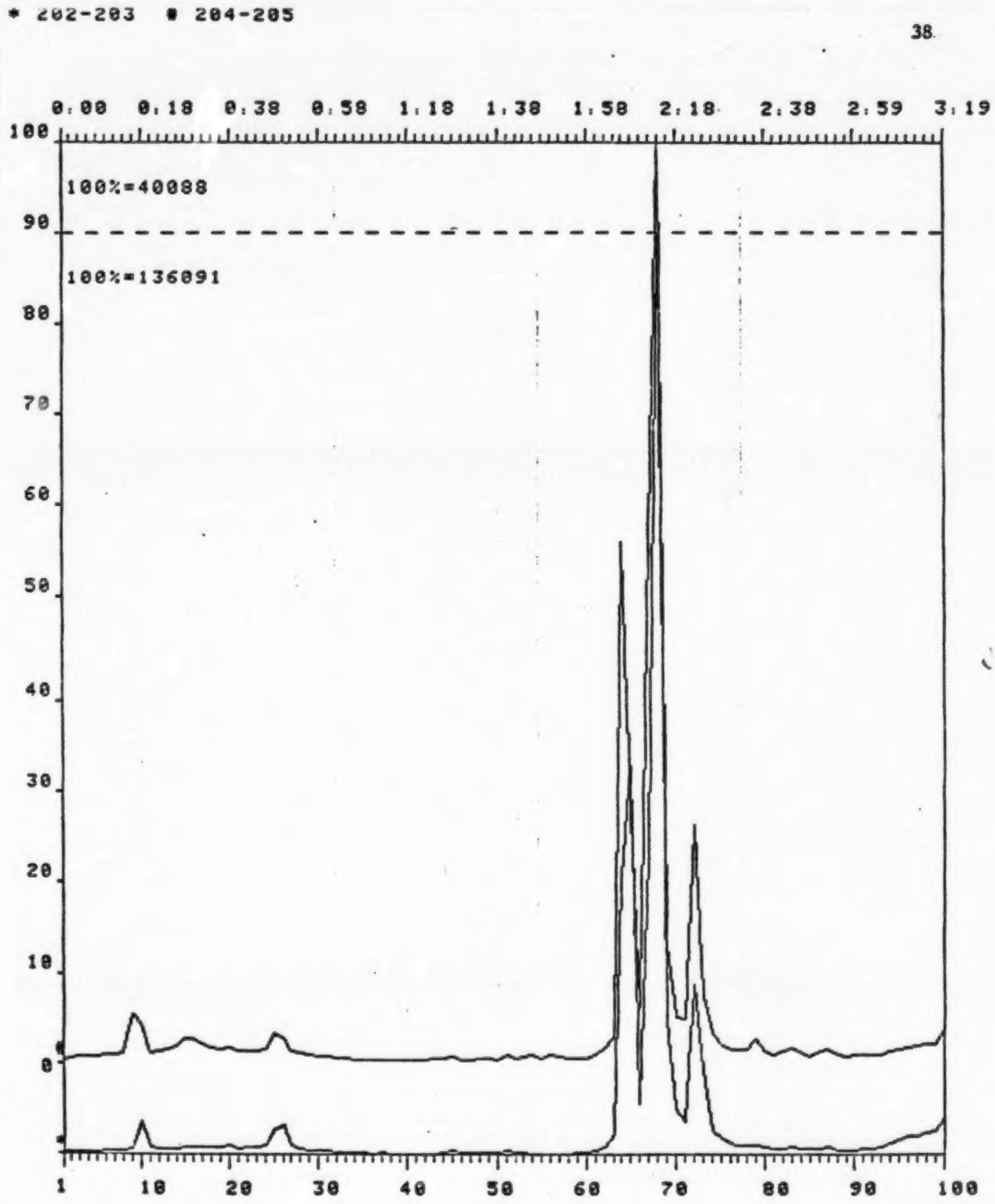


Figure C-11. Results of HRGC-MS analysis of ash sample 80-07-43 for monochlordibenzofurans.

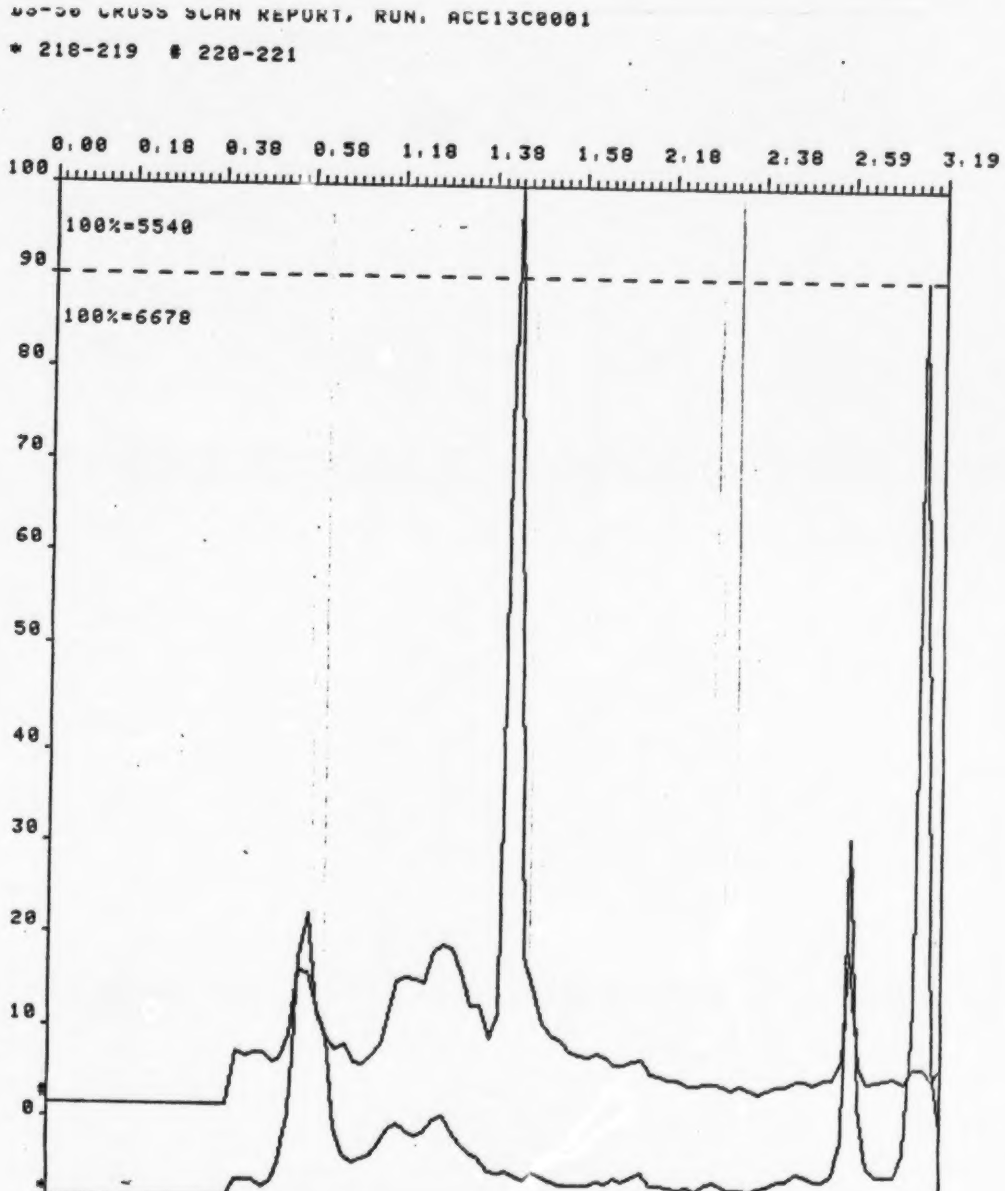


Figure C-12. Results of HRGC-MS analysis of ash sample 80-07-027-43 for monochlorodibenzo-p-dioxins.

12

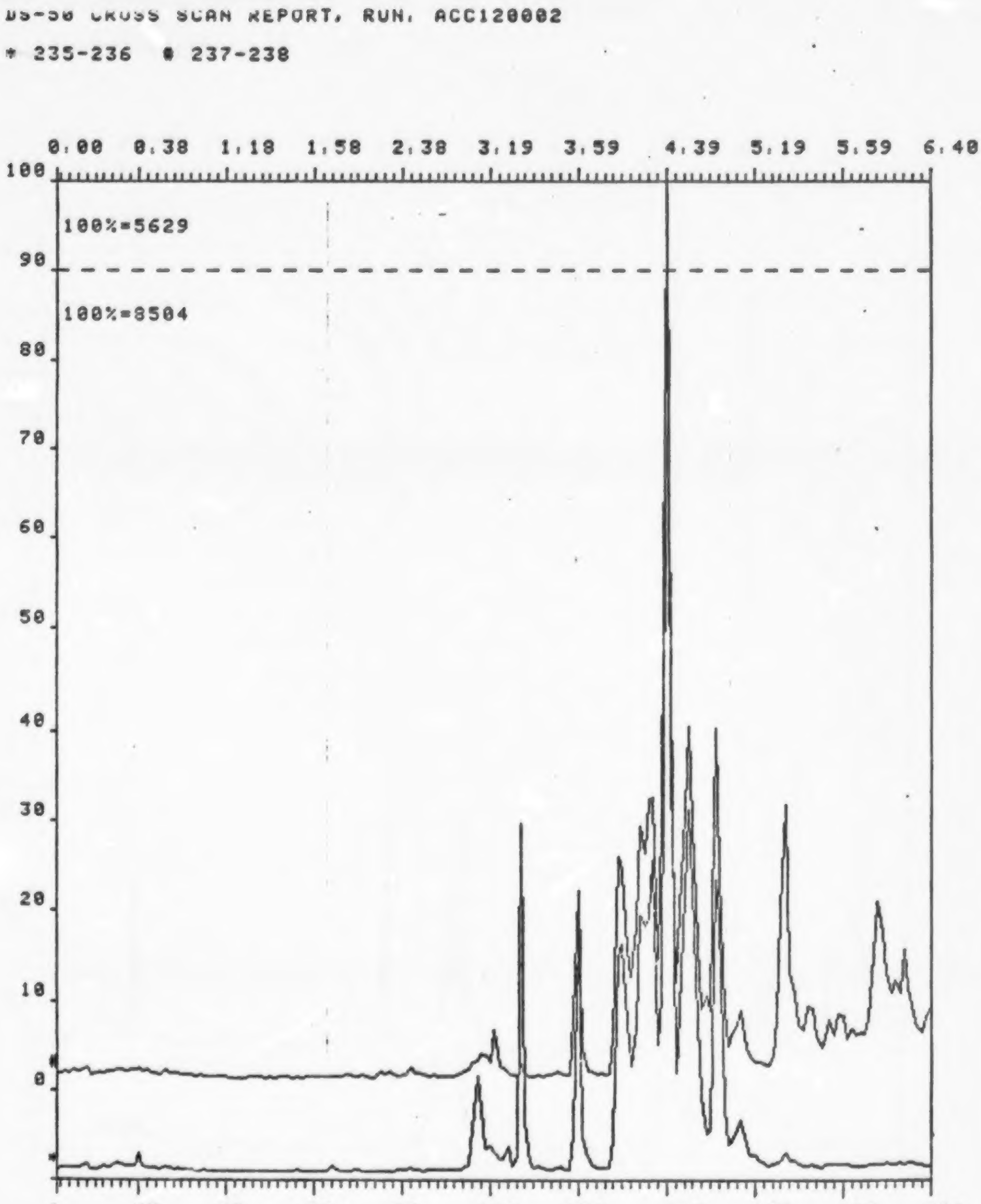


Figure C-13. Results of HRGC-MS analysis of ash sample 80-07-027-43 for dichlorodibenzofurans.

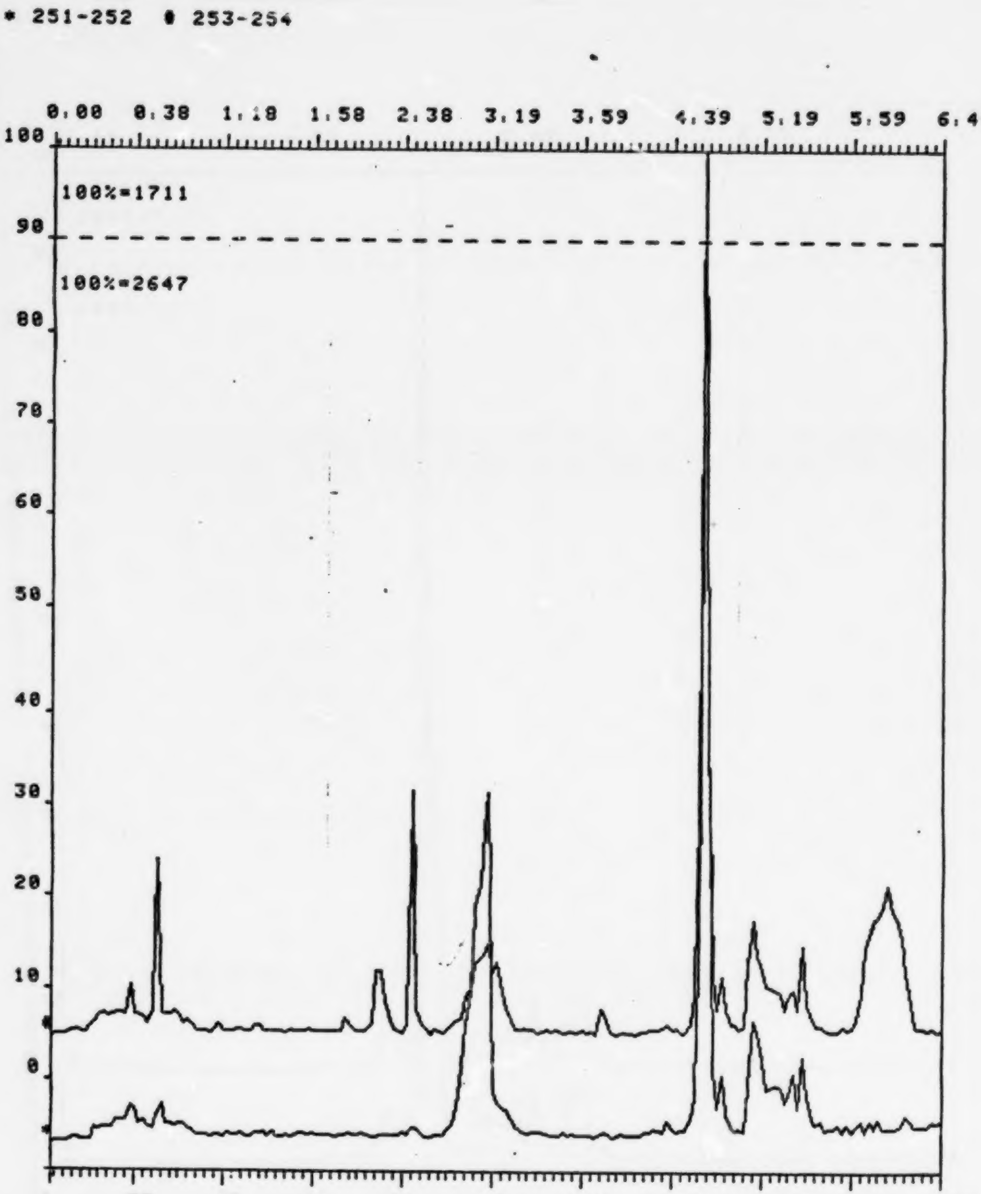


Figure C-14. Results of HRGC-MS analysis of ash sample 80-07-027-43 for dichlorodibenzo-p-dioxins.

14

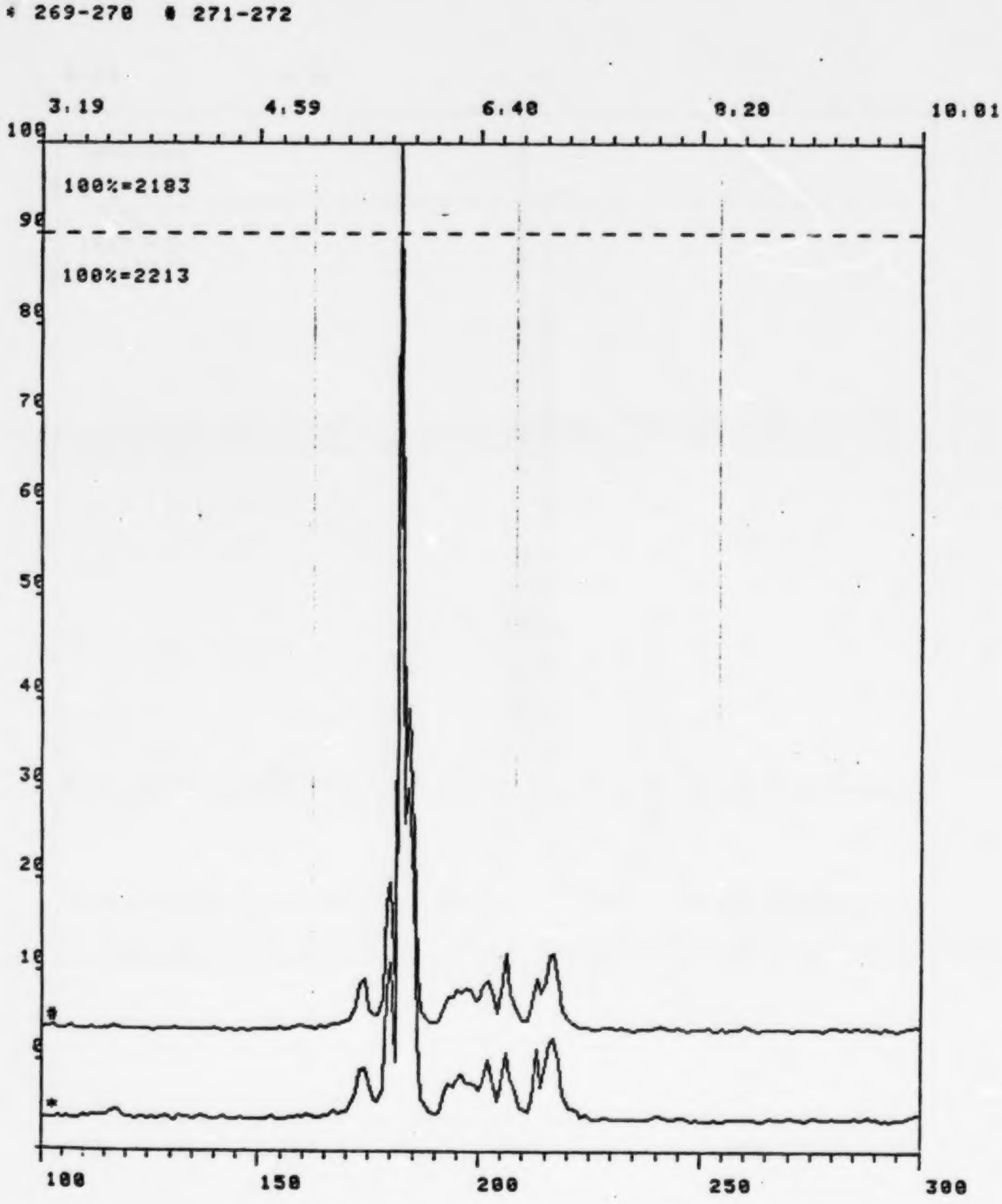


Figure C-15. Results of HRGC-MS analysis of ash sample 80-07-027-43 for trichlorodibenzofurans.

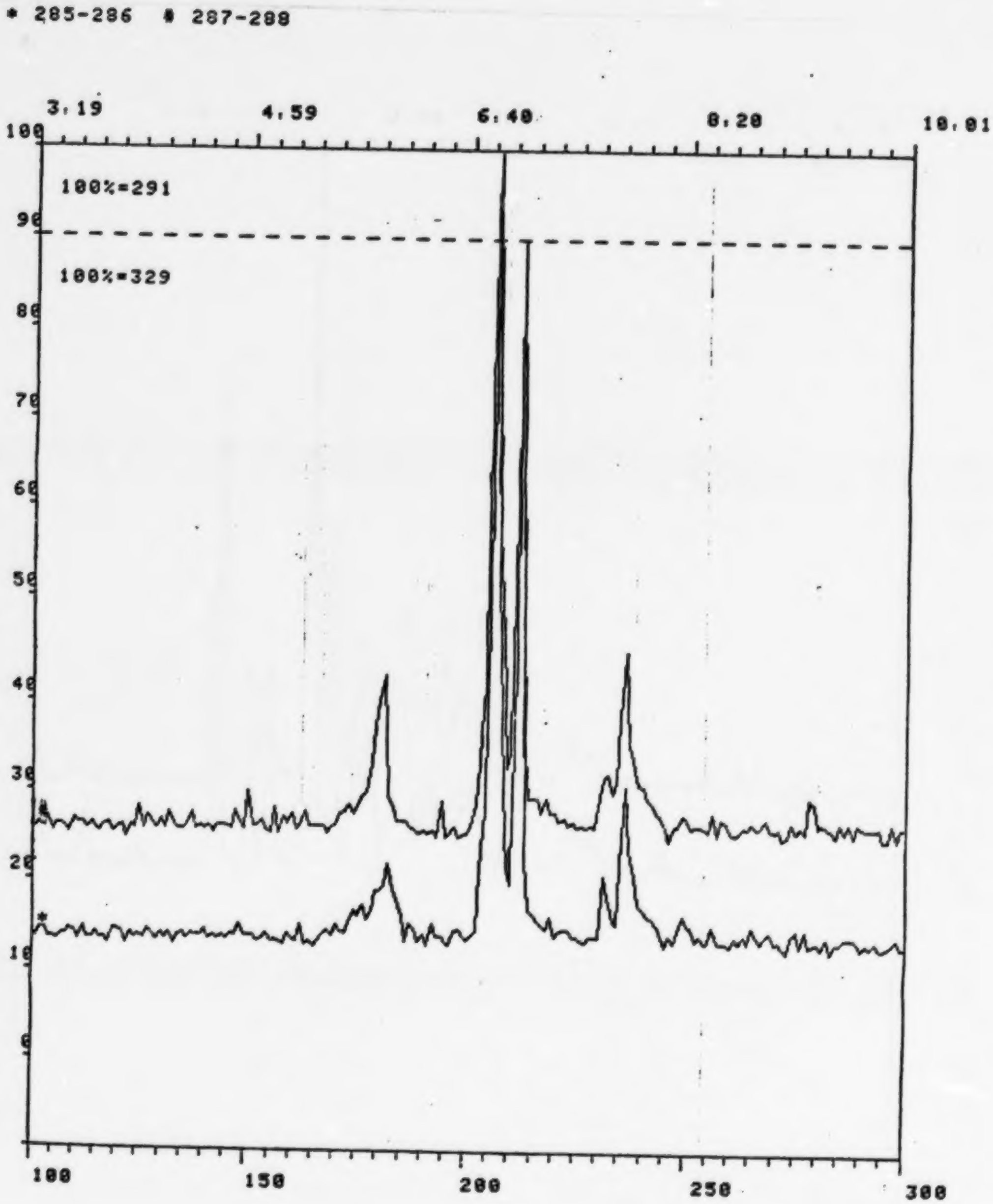


Figure C-16. Results of HRGC-MS analysis of ash sample 80-07-027-43 for trichlorodibenzo-p-dioxins.

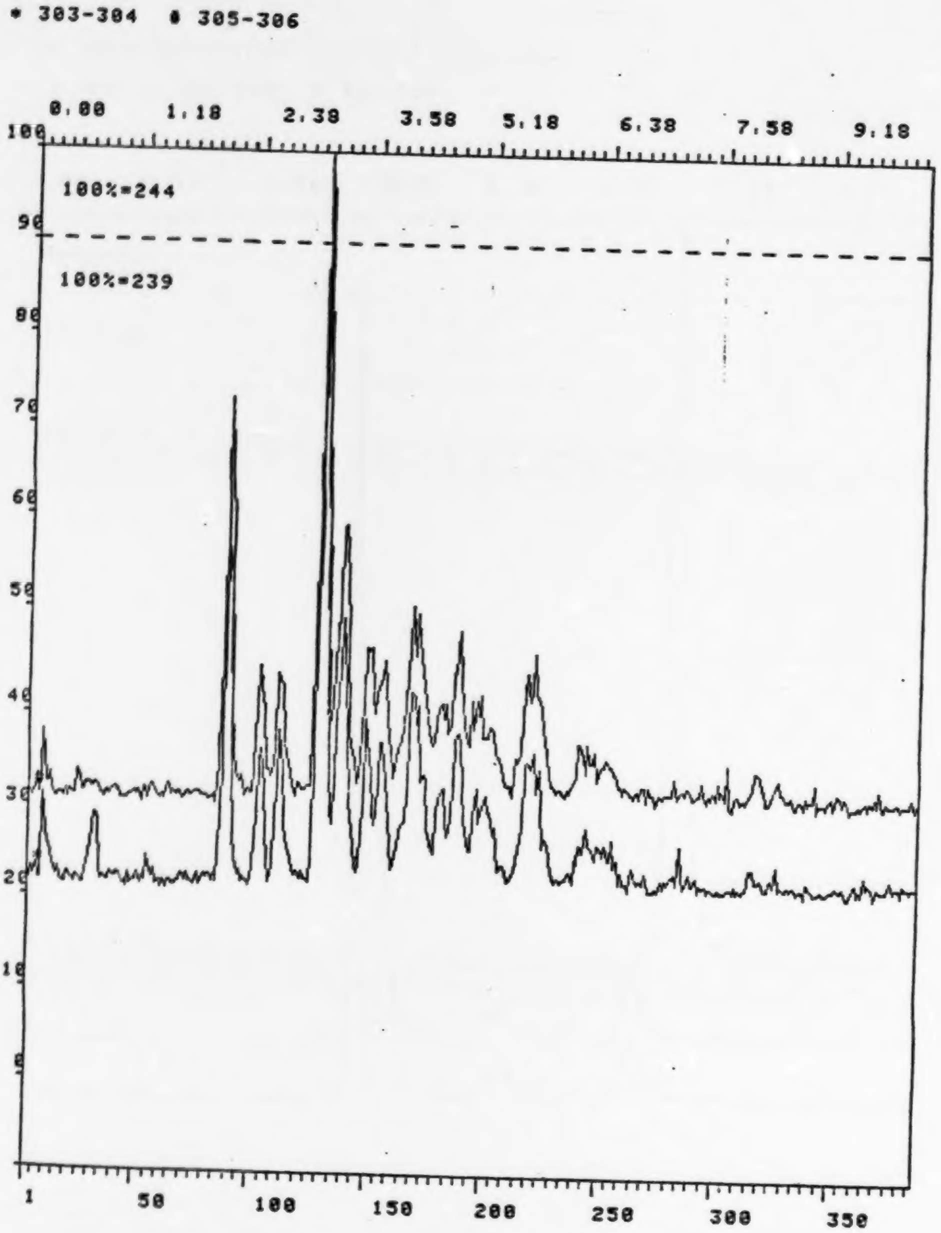


Figure C-17. Results of HRGC-MS analysis of ash sample 80-07-027-43 for tetrachlorodibenzofurans.

17

6

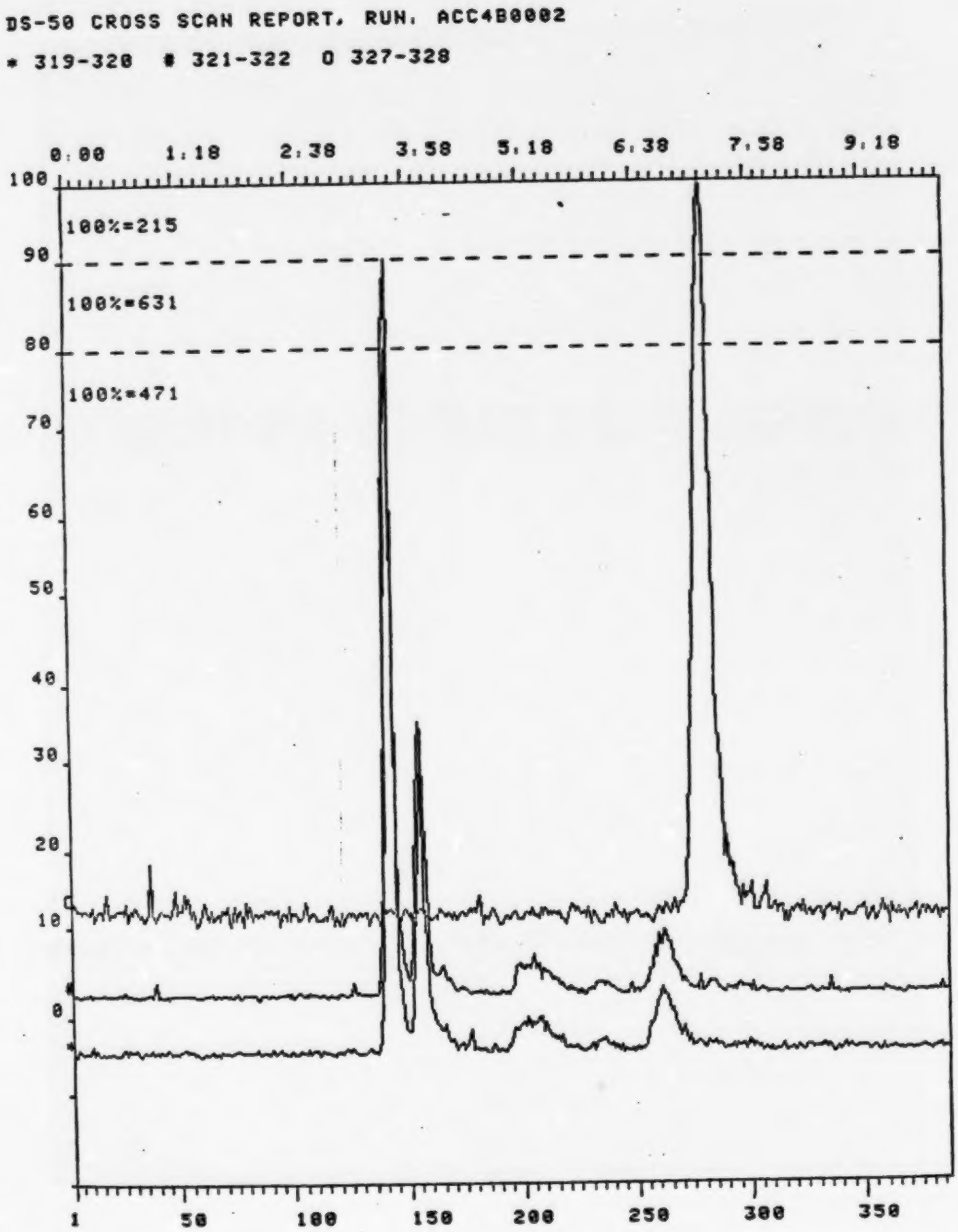


Figure C-18. Results of HRGC-MS analysis of ash sample 80-07-027-43 for tetrachlorodibenzo-p-dioxins.

18

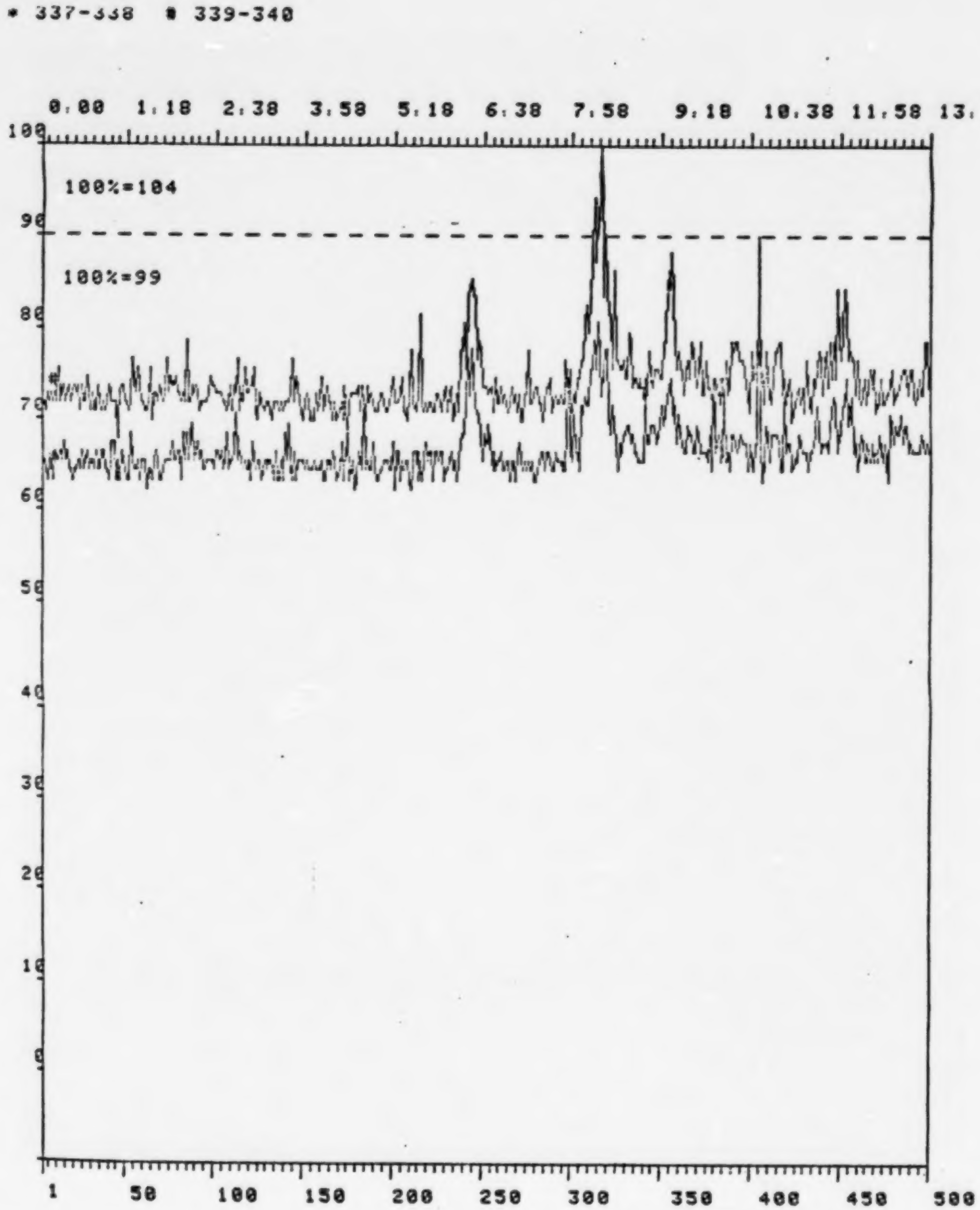


Figure C-19. Results of HRGC-MS analysis of ash sample 80-07-027-43 for pentachlorodibenzofurans.

19

4

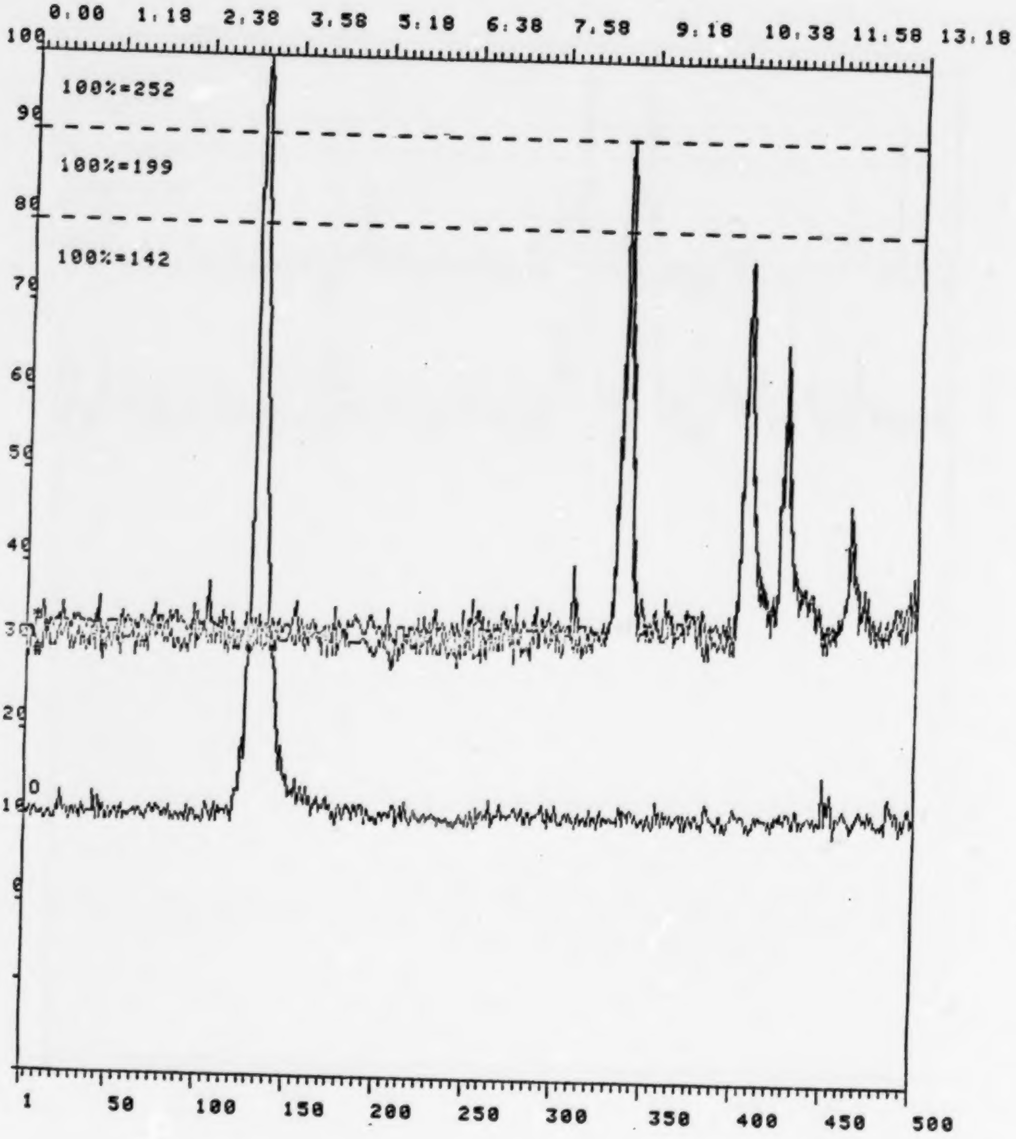


Figure C-20. Results of HRGC-MS analysis of ash sample 80-07-027-43 for pentachlorodibenzo-p-dioxins (results for the $^{37}Cl_4$-2,3,7,8-TCDD internal standard are also shown on lower trace).

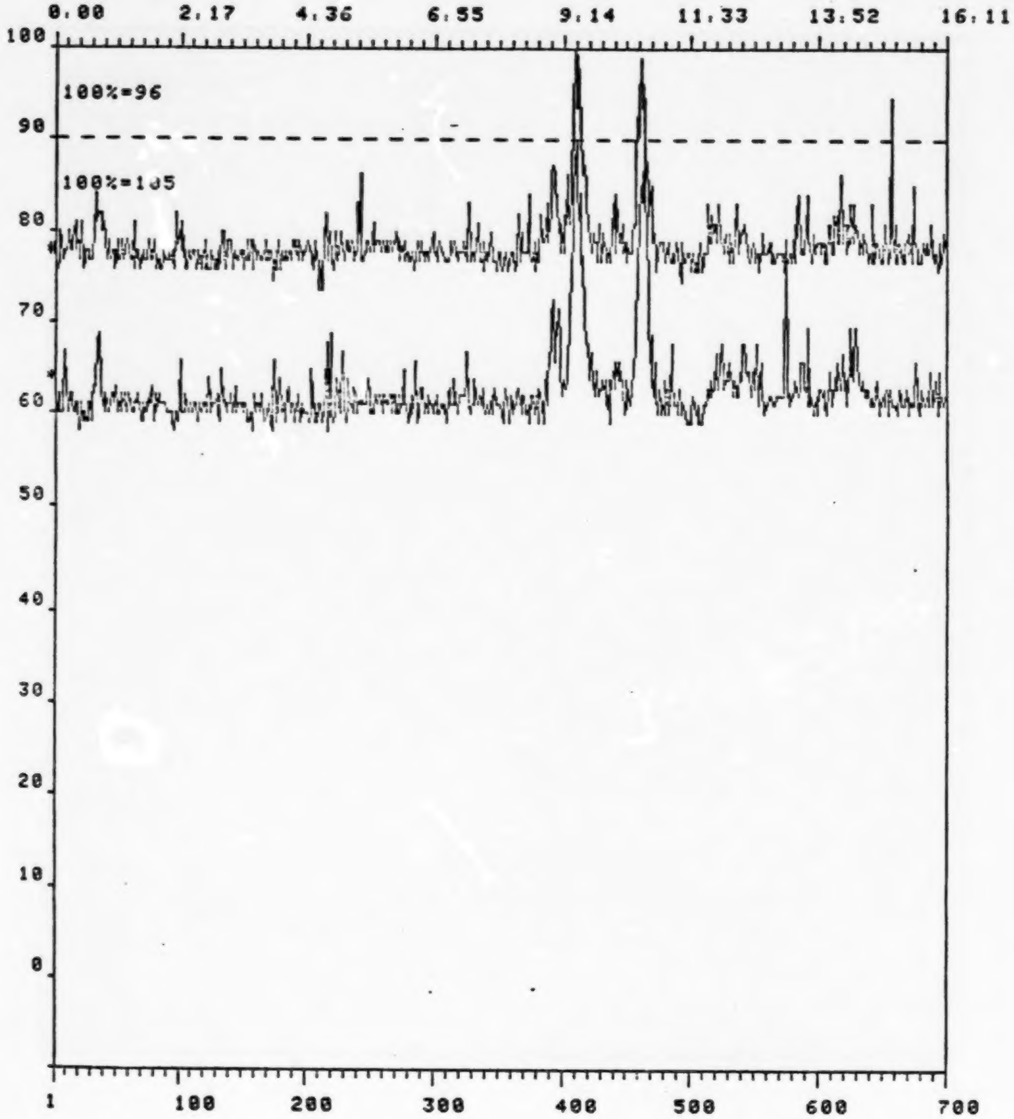


Figure C-21. Results of HRGC-MS analysis of ash sample 80-07-027-43 for hexachlorodibenzofurans.

21

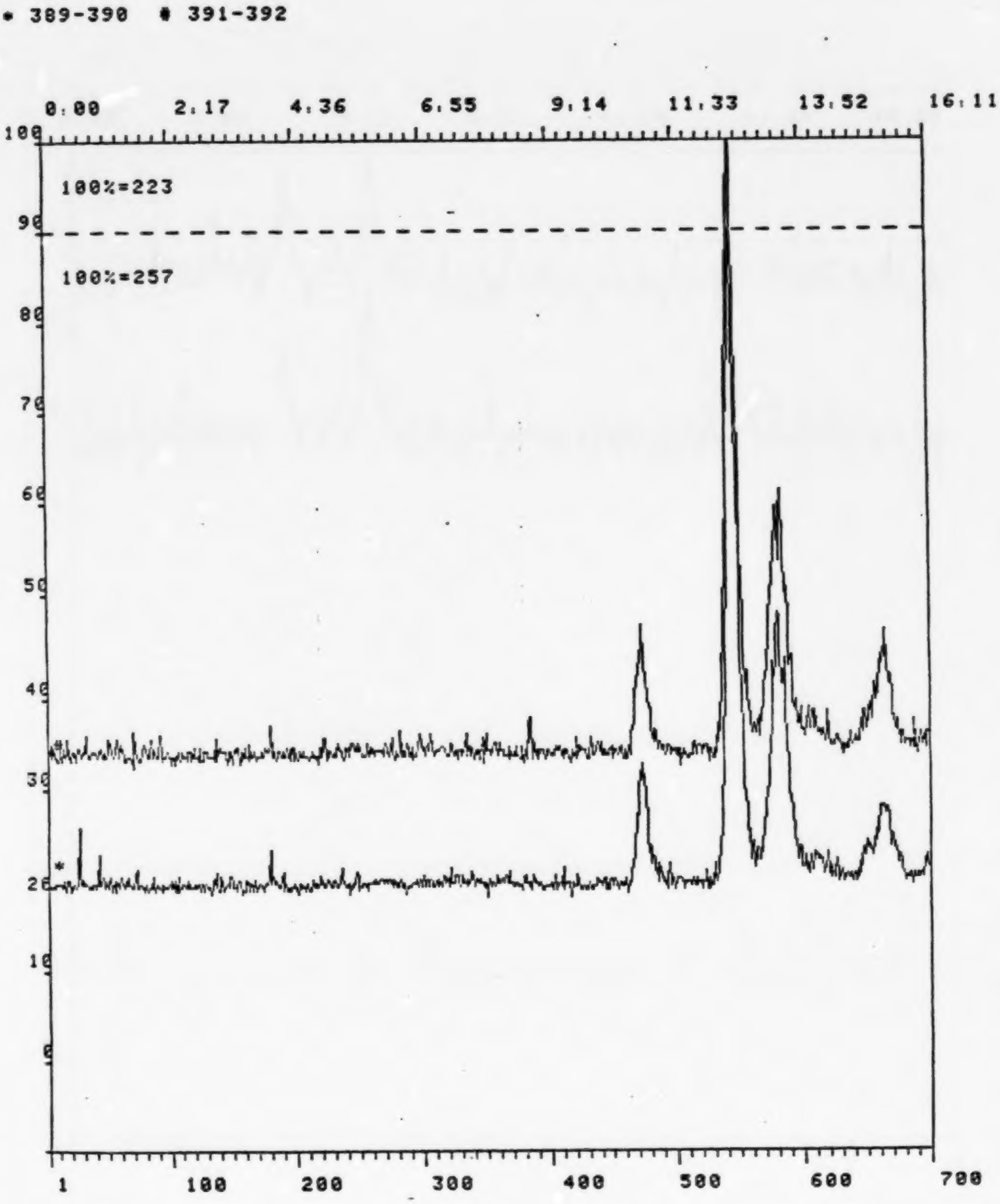


Figure C-22. Results of HRGC-MS analysis of ash sample 80-07-027-43 for hexachlorodibenzo-p-dioxins.

22

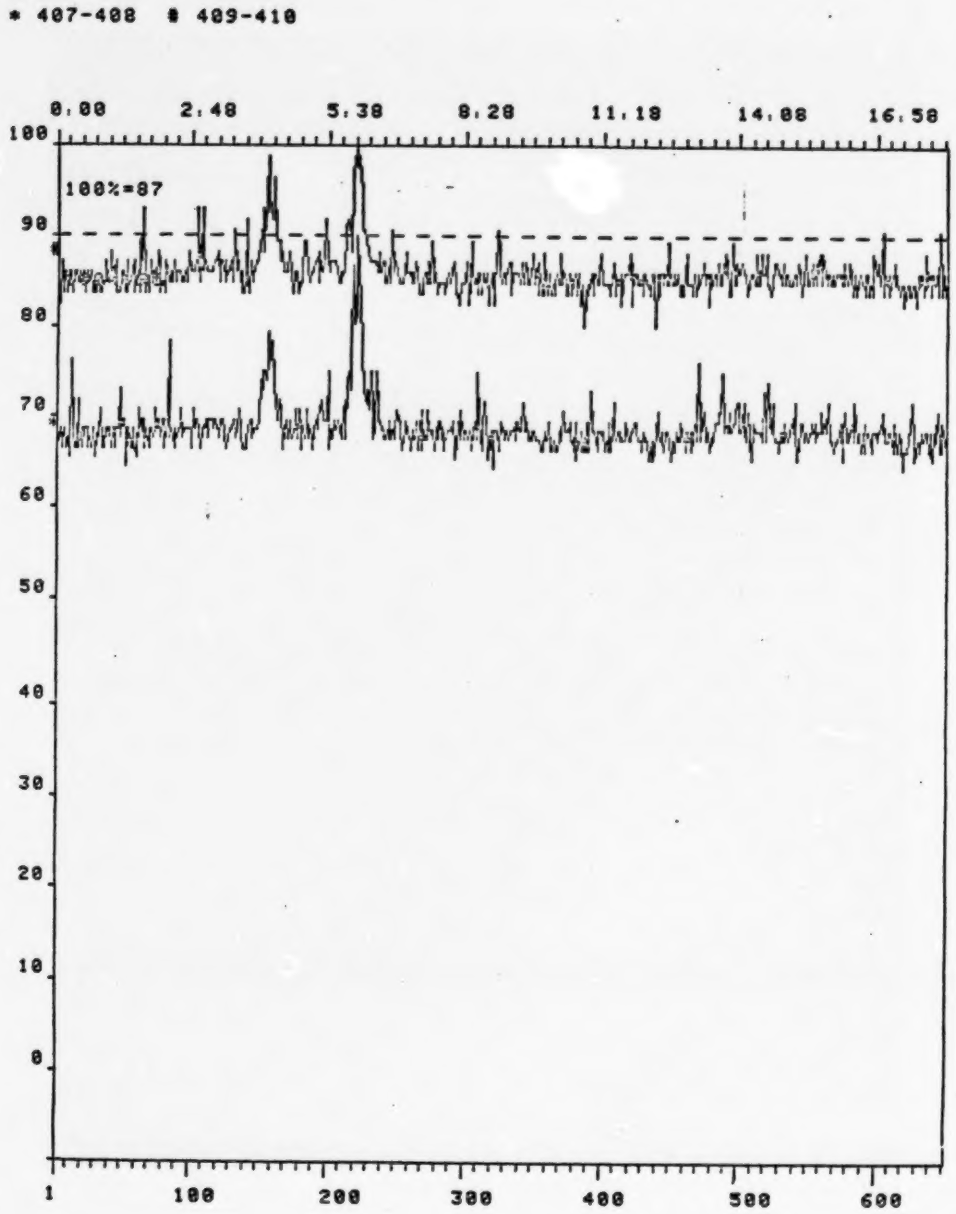


Figure C-23. Results of HRGC-MS analysis of ash sample 80-07-027-43 for heptachlorodibenzofurans.

23

V

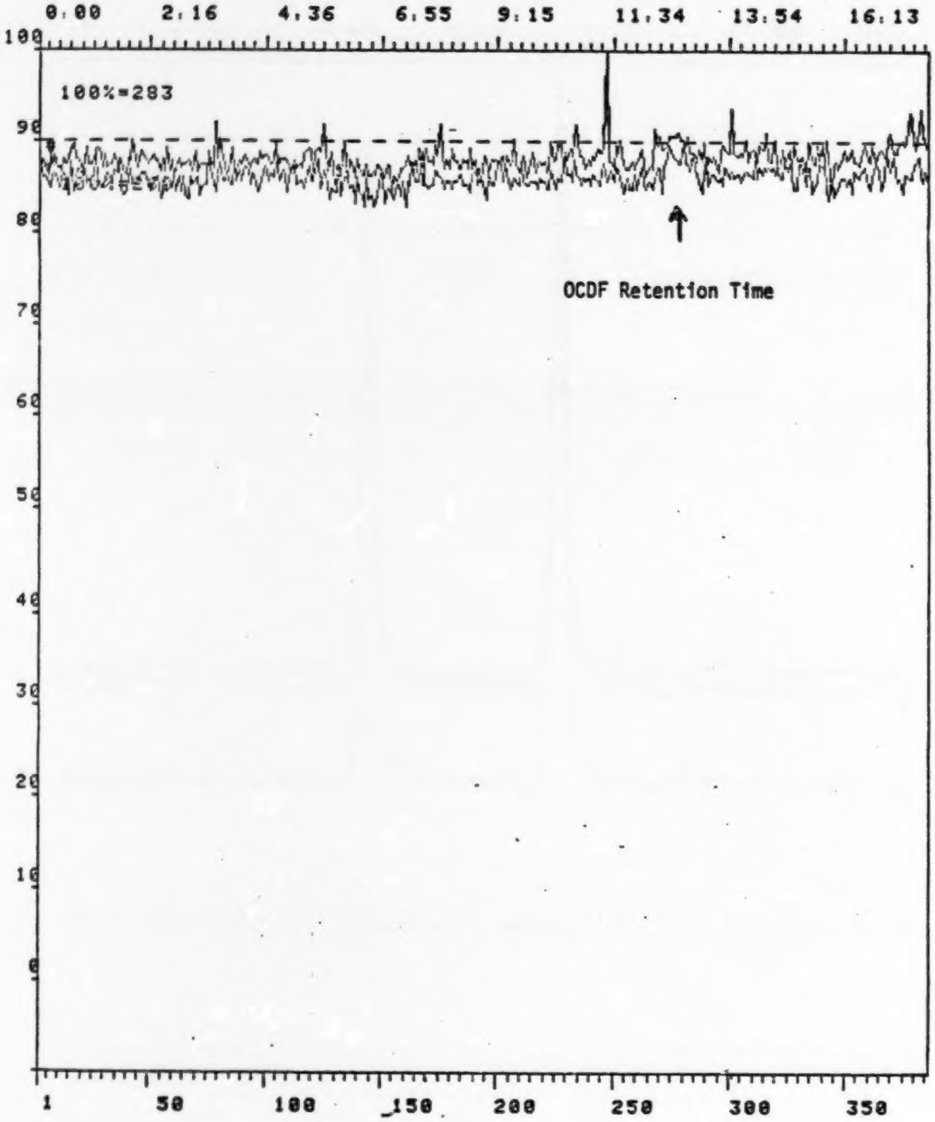


Figure C-24. Results of HRGC-MS analysis of ash sample 80-07-027-43 for octachlorodibenzofuran.

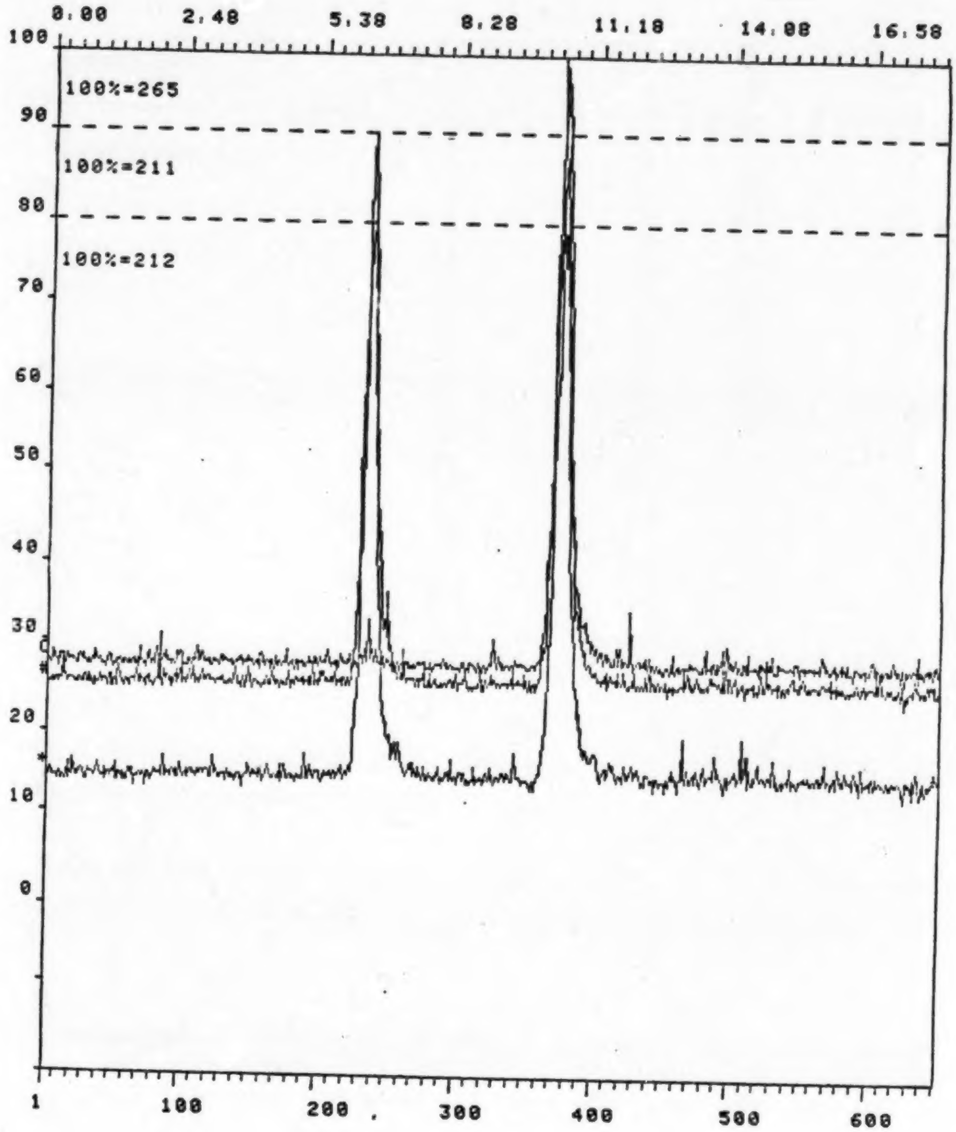


Figure C-25. Results of HRGC-MS analysis of ash sample 80-07-027-43 for heptachlorodibenzo-p-dioxins (results for the $^{37}Cl_4$-1,2,3,4,6,7,8-HpCDD internal standard are shown on center trace)

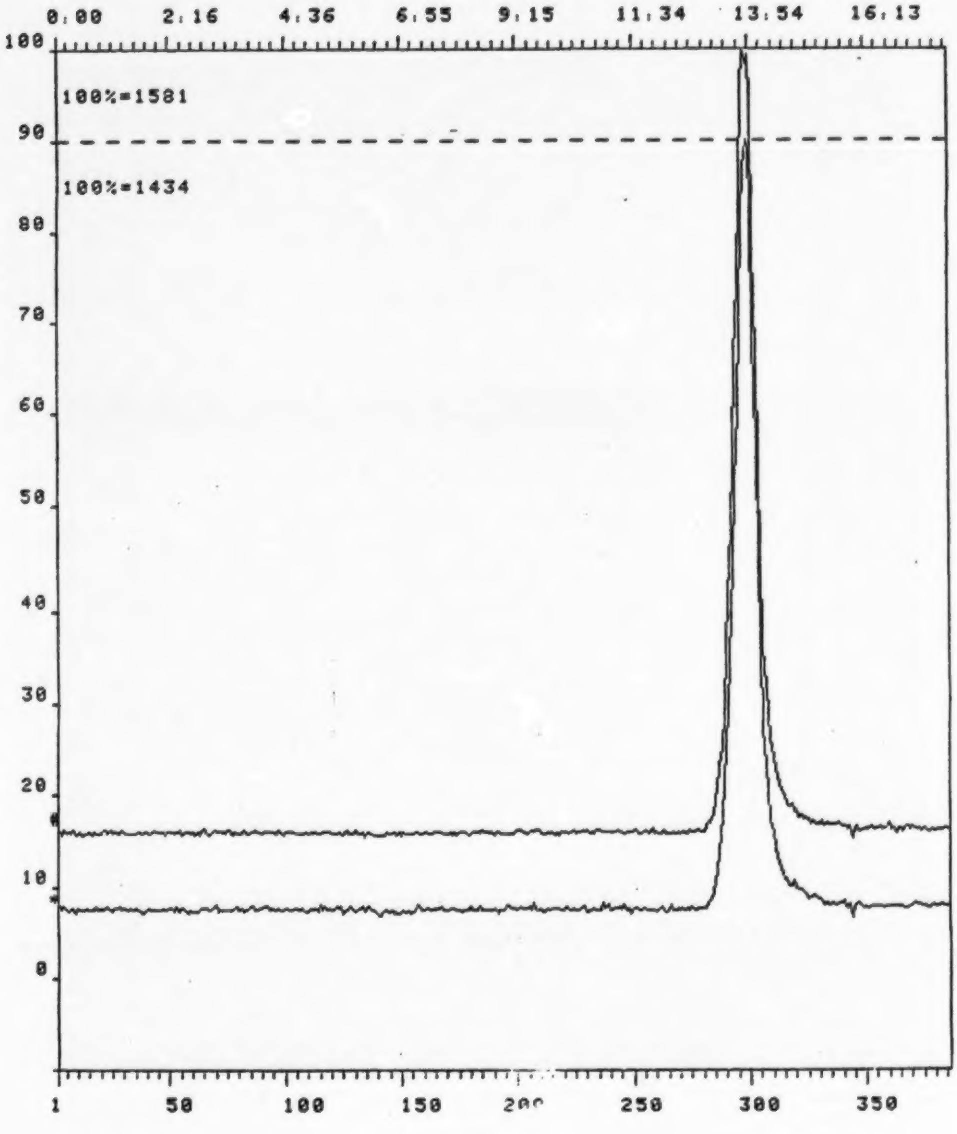
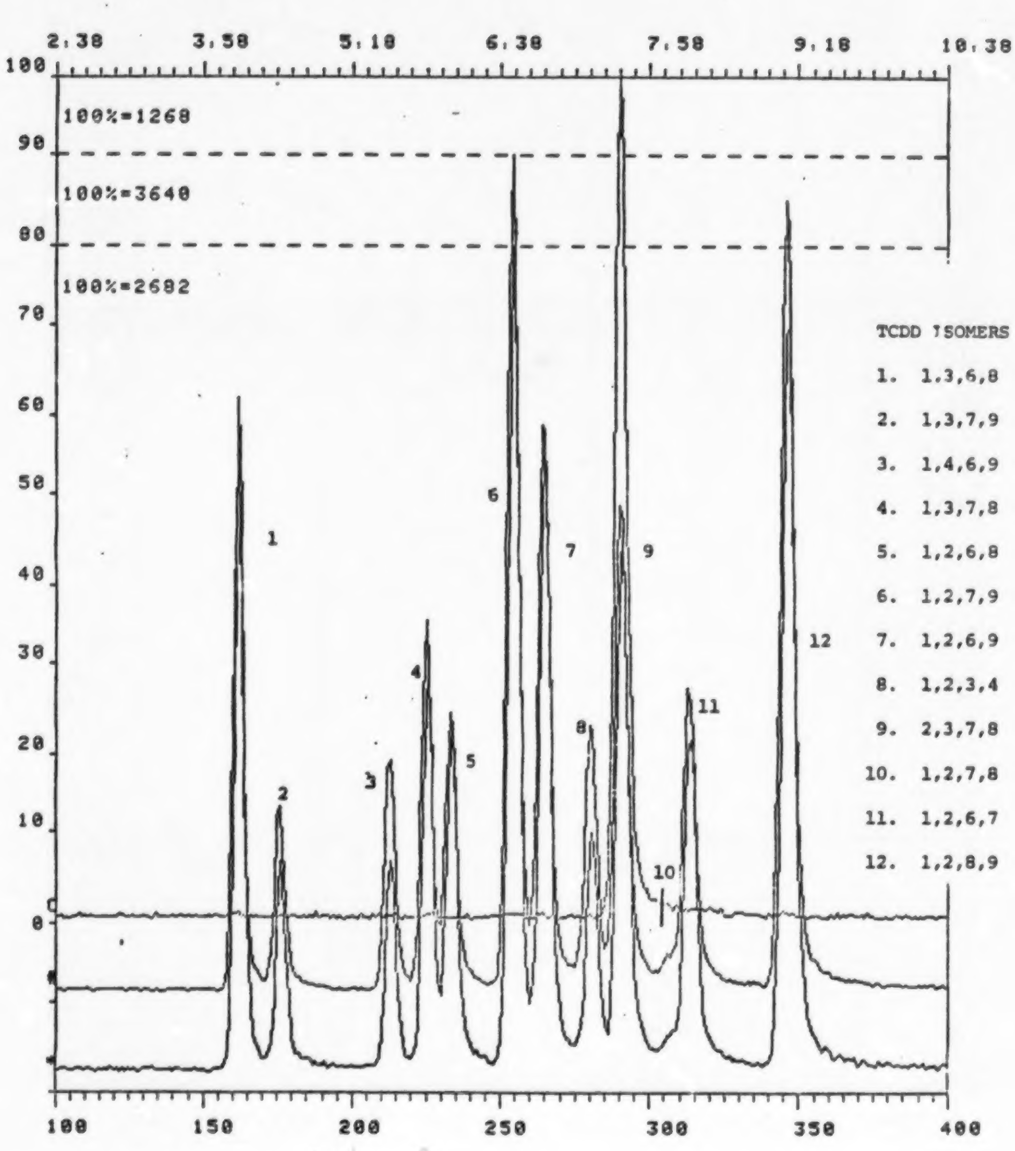


Figure C-26. Results of HRGC-MS analysis of ash sample 80-07-027-43 for octachlorodibenzo-p-dioxin.

26



Lab A

Figure C-27. Lab A -- multiple-ion mass chromatograms obtained for 12 isomer TCDD standard.

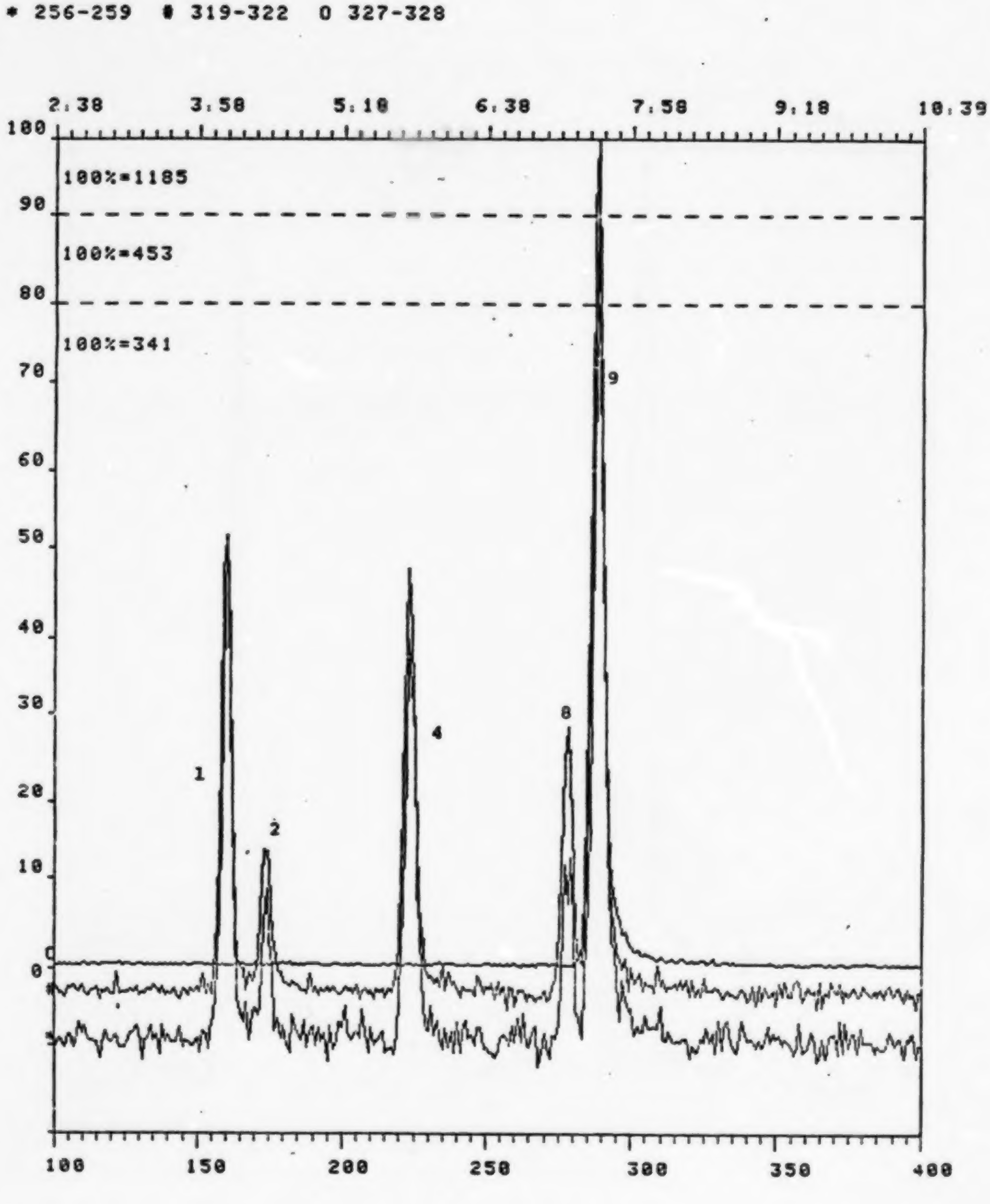


Figure C-28. Lab A — multiple-ion mass chromatograms obtained for 5-isomer TCDD standard.

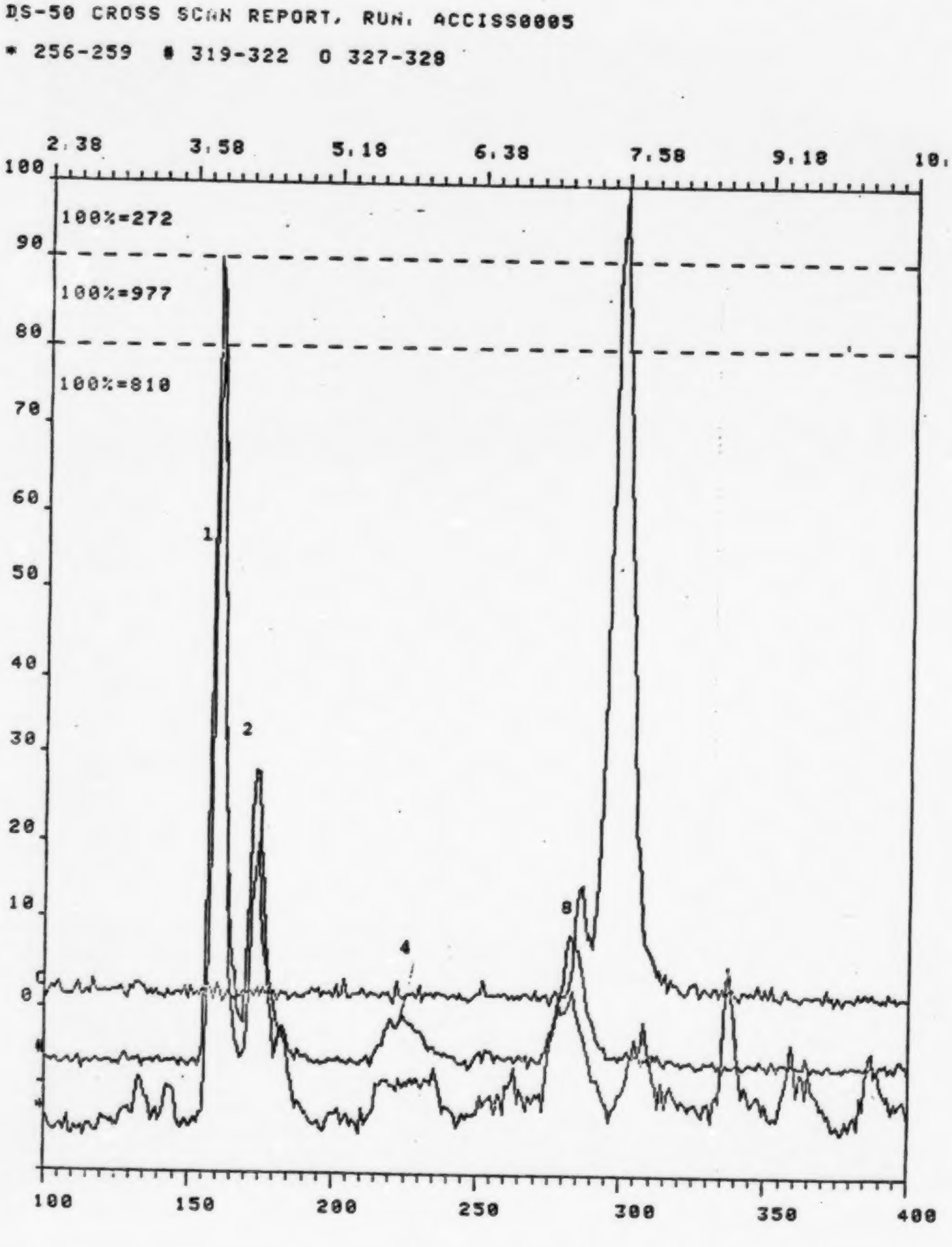


Figure C-29. Lab A — multiple ion mass chromatogram obtained for Acurex sample α80-07-027-43.

4

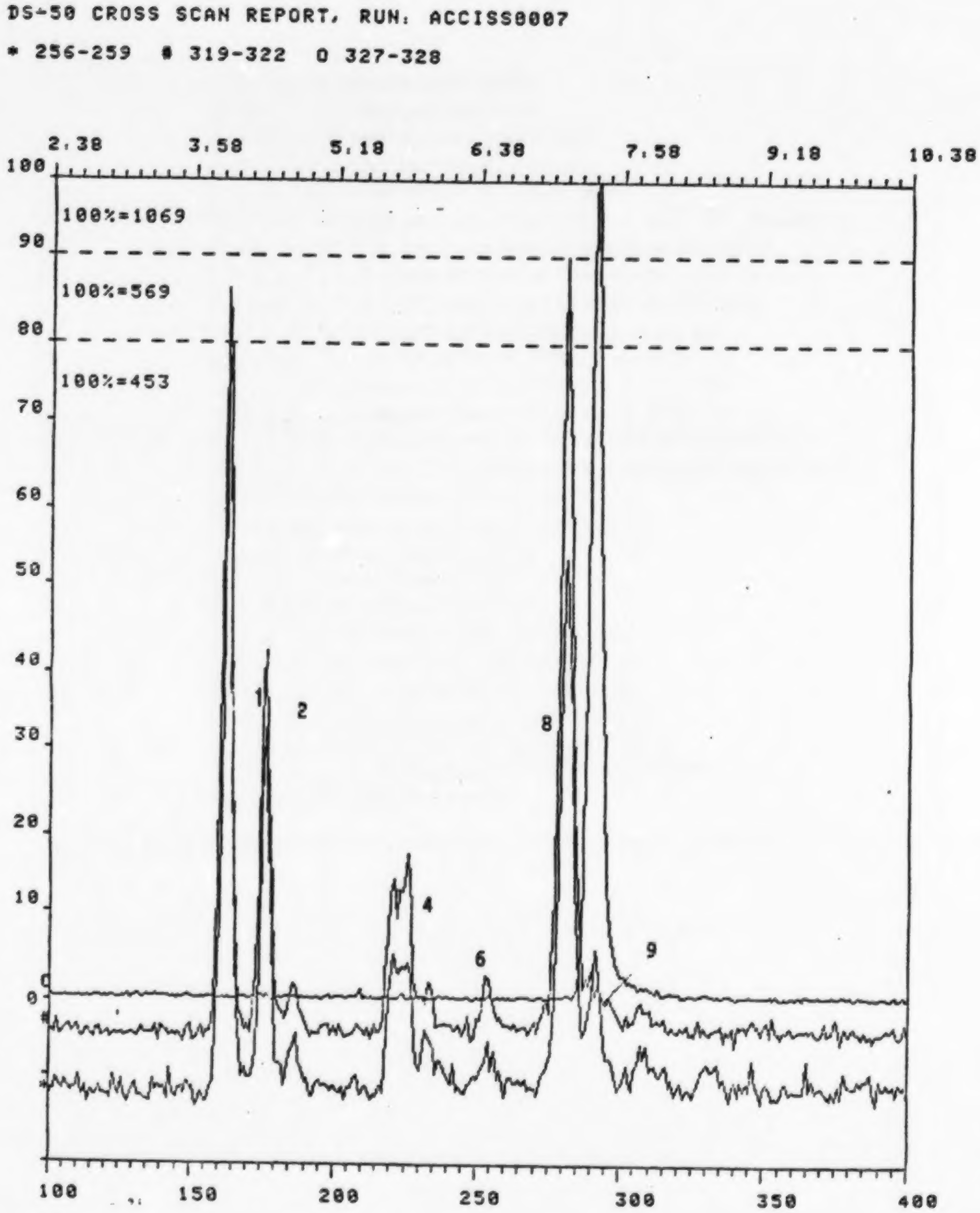


Figure C-30. Lab A -- multiple ion mass chromatograms obtained for Acurex sample α80-07-027-43.

TABLE C-15. LIST OF CHLORODIOXIN AND FURAN ISOMER STANDARDS CURRENTLY USED AT LABORATORY A

- 1-Chlorodibenzo-p-dioxin
- 2-Chlorodibenzo-p-dioxin
- 2,7-Dichlorodibenzo-p-dioxin
- 2,3-Dichlorodibenzo-p-dioxin
- 1,2,4-Trichlorodibenzo-p-dioxin
- Tetrachlorodibenzo-p-dioxins -- all 22 isomers
- $^{37}Cl_4$-2,3,7,8-Tetrachlorodibenzo-p-dioxin
- $^{13}C_4$-2,3,7,8-Tetrachlorodibenzo-p-dioxin
- $^{14}C_4$-2,3,7,8-Tetrachlorodibenzo-p-dioxin
- 1,2,3,7,8-Pentachlorodibenzo-p-dioxin
- 1,2,4,6,7,9-Hexachlorodibenzo-p-dioxin
- 1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin
- 1,2,3,4,6,7-Hexachlorodibenzo-p-dioxin
- 1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin
- $^{37}Cl_4$-1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin
- Octachlorodibenzo-p-dioxin
- $^{37}Cl_8$-Octachlorodibenzo-p-dioxin
- 2,4-Dichlorodibenzofuran
- 3,6-Dichlorodibenzofuran
- 2,8-Dichlorodibenzofuran
- 1,2,4-Trichlorodibenzofuran
- 1,2,4,8-Tetrachlorodibenzofuran
- 2,3,7,8-Tetrachlorodibenzofuran
- 1,2,4,7,8-Pentachlorodibenzofuran
- 1,2,4,6,7,9-Hexachlorodibenzofuran
- 1,2,3,4,6,8,9-Heptachlorodibenzofuran
- Octachlorodibenzofuran

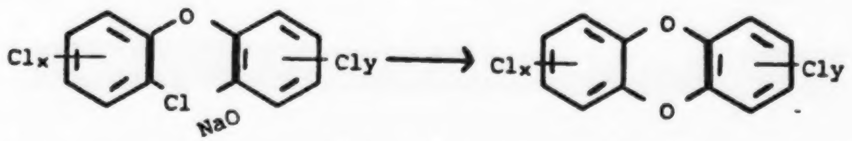
C.5.1 Samples 07-027-18 (Flyash) and 07-027-10 (Bottom Ash)

These samples were subjected to Soxhlet extraction for 24 hours with benzene after which the benzene was removed and replaced with petroleum ether. The petroleum ether was then concentrated to about 1 ml and cleaned up using a Woelm basic alumina column which was first eluted with 10 ml of 2 percent methylene chloride/hexane and the fraction discarded. The dioxins and dibenzofurans were then eluted with 50 percent dichloromethane/hexane. This eluate was concentrated to 200 μl and submitted for analysis.

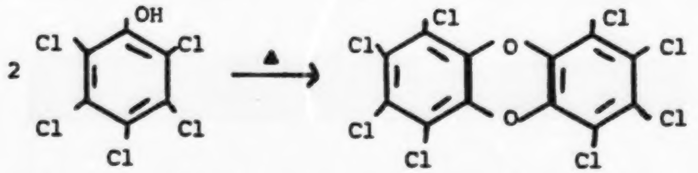
C.5.2 Samples 11-043-80 and 10-015-3 (Pond Sludges) and 07-027-03 (ENTA)

These samples were shaken with 10 percent methylene chloride/hexane and the sorbent placed on the head of a column (30 cm x 18 mm) which had been wet packed with 40 ml of Fisher A-540 alumina deactivated with 5 percent H_2O and topped with 2 gm of Na_2SO_4. The column was then eluted with 150 ml of 10 percent methylene chloride in hexane directly into a Kuderna-Danish apparatus where the column of solvent was reduced to ~20 ml. This extract was then subjected to washes with 20 percent KOH, water, concentrated sulfuric acid and again, water. The extract was then dried over sodium sulfate and concentrated to about 1 ml prior to Woelm alumina column chromatography as described above.

The data are presented in Tables C-16 and C-17. On several of the samples the recoveries for the monochlorodioxin in the spiked samples are quite low or nonexistent. This is due to the washes with concentrated sulfuric acid. A cleanup this severe was necessitated since the samples contained interfering compounds at concentrations many times higher than the dioxins. Sulfonation has been found to be an effective way of removing many of the compounds so it was employed even at the risk of losing the monochlorodioxin. One other concern arising from the use of such severe cleanup procedures is the possibility of dioxins being formed by the cyclization of dioxin precursors by any of several possible mechanisms:



or the almost quantitative yield of octachlorodibenzodioxin formed directly from the heating of pentachlorophenol:



Since these samples were all from various wood treating facilities, it was expected that they could contain pentachlorophenol and various ortho-chlorophenols in high concentration relative to any dioxins present.

TABLE C-16. DIOXINS IN SAMPLES - Ng/g

Sample	MCDD	DCDD	T_rCDD	TCDD	PCDD	HCDD	H_pCDD	OCDD
07-027-18 (flyash)	ND	ND	ND	ND	ND	ND	ND	ND
07-027-18 Spike	ND	51	62	60	122	237	117	312
Spike level	234	101	119	107	223	378	217	452
Recovery	-	50%	52%	56%	55%	63%	54%	69%
Lower detection limit	117	51	60	54	112	189	109	226
07-027-10 (bottom ash)	ND	ND	ND	ND	ND	ND	ND	298
07-027-10 Replicate	ND	ND	ND	ND	ND	ND	ND	381
07-027-10 Spike	ND	45	65	71	153	275	198	420
Spike level	204	88	104	94	195	330	189	395
Recovery	-	51%	62%	75%	79%	83%	104%	106%
Lower detection limit	102	44	52	47	98	165	95	198
11-043-80 (pond sludge)$^{P+B}$	ND	ND	ND	ND	ND	ND	ND	2102
11-043-80 Spike	1142	325	272	238	558	959	819	2598[a]
Spike level	855	370	435	391	816	1381	791	1652
Recovery	133%	88%	63%	61%	68%	69%	103%	a
Solvent blank	ND	ND	ND	ND	ND	ND	ND	ND
Lower detection limit	430	185	218	196	408	691	396	826
10-015-3 (pond sludge)$^{P+A}$	ND	ND	ND	38[b]	ND	ND	586	2209
10-015-3 Replicate	ND	ND	ND	38[b]	ND	ND	491	2060
10-015-3 Spike	ND	275	203	148	479	756	446	666
Spike level	491	213	250	225	469	794	455	950
Recovery	-	129%	81%	66%	102%	91%	98%	a
10-015-3 Spike	482	576	496	419	891	1484	963	1800
Spike level	983	426	500	450	938	1588	910	1900
Recovery	49%	135%	99%	93%	95%	93%	106%	95%
Lower detection limit	246	107	125	113	235	397	228	475
07-027-03 (Penta)	c	c	c	c	c	1538	17095	>17095

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[a] Recovery not reported since background OCDD present at levels greater than the spike.

[b] Probably 1,3,6,8-TCDD.

[c] Interferences too large to allow quantitation.

ND = None detected below lower detection limit.

TABLE C-17. DIBENZOFURANS IN SAMPLES - Ng/g

Sample	mono	di	tri	tetra	penta	hexa	hepta	octa
07-027-18 (flyash)	ND	54	ND	ND	ND	ND	ND	ND
07-027-18 Replicate	29	64	ND	ND	ND	ND	ND	ND
07-027-18 Spike	ND	49	ND	ND	ND	ND	ND	ND
Spike level	54	95	103	67	154	263	57	163
Recovery	-	51%	-	-	-	-	-	-
Lower detection limit	27	48	52	34	77	132	29	163
07-027-10 (bottom ash)	ND	ND	ND	ND	ND	ND	ND	ND
07-027-10 Replicate	ND	ND	ND	ND	ND	ND	ND	ND
07-027-10 Spike	ND	60	61	49	119	213	52	127
Spike level	47	83	90	58	135	229	49	142
Recovery	-	72%	67%	84%	88%	93%	106%	90%
Lower detection limit	24	42	45	29	68	115	25	71
11-043-80 (pond sludge)	177[a]	a	586	ND	ND	ND	309	294
11-043-80 Spike	245	330	383	253	628	1222	279	628
Spike level	330	590	640	410	950	1620	350	1010
Recovery	74%	56%	60%	62%	66%	75%	80%	62%
Solvent blank	ND	ND	ND	ND	ND	ND	ND	ND
Lower detection limit	165	295	320	205	475	810	175	505
10-015-3 (pond sludge)	ND	365[b]	ND	ND	ND	ND	ND	ND
10-015-3 Replicate	ND	319[b]	ND	ND	ND	ND	ND	ND
10-015-3 Spike	-	441	278	193	459	738	173	364
Spike level	330	590	640	410	950	1620	350	1010
Recovery	-	75%	43%	47%	48%	40%	50%	36%
Solvent blank	ND	ND	ND	ND	ND	ND	ND	ND
Lower detection limit	110	197	213	137	317	540	117	337
07-027-03 (Penta)	255	ND	ND	ND	929	3088	3499	5471
07-027-03 Replicate	105	3547	ND	ND	905	2289	2721	3850
07-027-03 Spike	221	2992	2594	531	1061	901	-	203
Spike level	429	762	824	533	1233	2100	452[c]	1305[c]
Recovery	51%	392%	315%	99%	86%	43%	c	c

[a] Interferences.

[b] Isomers other than those used to spike sample.

[c] Recovery not given since spike levels were significantly below the level present in the sample.

ND - None detected below lower detection limit.

The initial cleanup step of chromatographing the samples on a neutral alumina column was included to eliminate the possibility of artifact formation by removing the possible precursors prior to acid or base washes.

It was not possible in all cases to adhere to a strict QA/QC program due primarily to the inadequate amount of sample received. Whenever possible, however, QA/QC Method MCR Method no. 7 was followed without exception.

The samples were analyzed using MRC Method no. 1 with the exception that a 1 percent Dexsil 300 column was substituted for the 3 percent Dexsil 400 column.

In addition, each sample was fortified with $^{13}C_{12}$-TCDD prior to workup to serve as an internal standard.

C.6 LABORATORY C ANALYSIS

C.6.1 Extraction and Clean-Up Procedures in Flyash Analyses

In a recent publication Lustenhouwer, et al., have compared the efficiency of various solvents to extract PCDDs and PCDFs from flyash and other particulate matter. The data reported in Table 2, p. 503, clearly shows that the highest efficiency was found for Soxhlet extraction with toluene on acid treated material. In an unpublished study Lab C reported that the temperature of the solvent in the Soxhlet extractor is also of importance, the efficiency was found to increase with increasing temp.

In the Lab C analyses an extraction procedure based on acid treatment was used followed by Soxhlet extraction with hot tuluene for 36 hrs. This should be an optimal procedure for the extraction of PCDDs and PCDFs.

The extraction procedure was followed by a clean-up on an alumina column resulting in a fraction where PCDDs and PCDFs could be determined without interferring artifacts.

C.6.2 Separation, Quantification and Confirmation

In the Lab C analyses a 55 m Silar 10 c glass capillary column was used for the separation of the PCDDs and PCDFs. The lab recently reported using column to separate 2,3,7,8-tetra-CDD from all other 21 TCDD isomers, thus allowing an unambigous identification of the highly toxic 2,3,7,8-isomer.

The quantification is based on mass fragmentography and comparison with calibration curves of known amounts of 2,3,7,8-tetra-CDD, 1,2,3,7,8-hexa-CDD and octa-CDD, 2,3,7,8-tetra-CDF, 1,2,3,4,7,8,-hexa-CDF and octa CDF.

Positive identification of PCDD and PCDF isomers was based on the following requirements:

a) Identical retention times with synthetic standards on one (or two) glass capillary columns.

b) Complete mass-spectra showing the expected chlorine-clusters for the parent ions and the expected fragmentation.

The mass fragmentograms of the plant C ash sample 80-07-027-18 is given in Figures C-31 and 32. A study of these figures reveals:

a) All the major peaks co-elute with synthetic standards.

b) The possibility of analyzing false positives is very very small, $p < 10^{-10}$.

c) The same pattern of PCDDs is observed as in other "normal" flyash samples, see Figure C-33. This indicates the same precursors, namely chlorophenols.

d) 2,3,7,8,-tetra-CDD is a very very minor peak.

e) > 90Δ of the PCDDs are lower chlorinated congeners than octa-CDD.

f A difference in the pattern of PCDFs is observed compared to other "normal" flyash samples, see Figure C-34.

In the analytical system used by Lab A a peak from the ash extract is apparently co-eluting with the authentic 2,3,7,8-TCDD standard.

Lab C personnel believe they can unambiguously separate the 2,3,7,8-isomer from the other 21 isomers. Consequently they have already performed a deeper study of possible thermal isomerization of 2,3,7,8-TCDD.

Lab C analyses are in disagreement with the Lab A analyses. Figure C-32 clearly shows that 2,3,7,8-TCDD is not present in these ash samples.

C.6.3 The Pattern of PCDDs

The same pattern of PCDD is observed in Lab C data as in other European flyash samples, see Figure C-33. Chlorinated phenols are the precursors to the PCDDs found in all these samples. Lab C has also observed that more than 90Δ of the PCDDs are lower chlorinated more than the expected OCDD. This is due to a nonspecific dechlorination of OCDD previously studied by Rappe et al.

C.6.4 The Pattern of PCDFs

The pattern of PCDFs observed is slightly different than that found in "normal" flyash analyses indicating different precursors. In the normal fly ash PCBs are the major precursors, in the Acurex samples the precursors are believed to be impurities in the commercial Penta, Figure C-34.

Standard isomers for PCDF's and PCDD's used by Laboratory C included at least one isomer for each monomer and included 100 individual isomers.

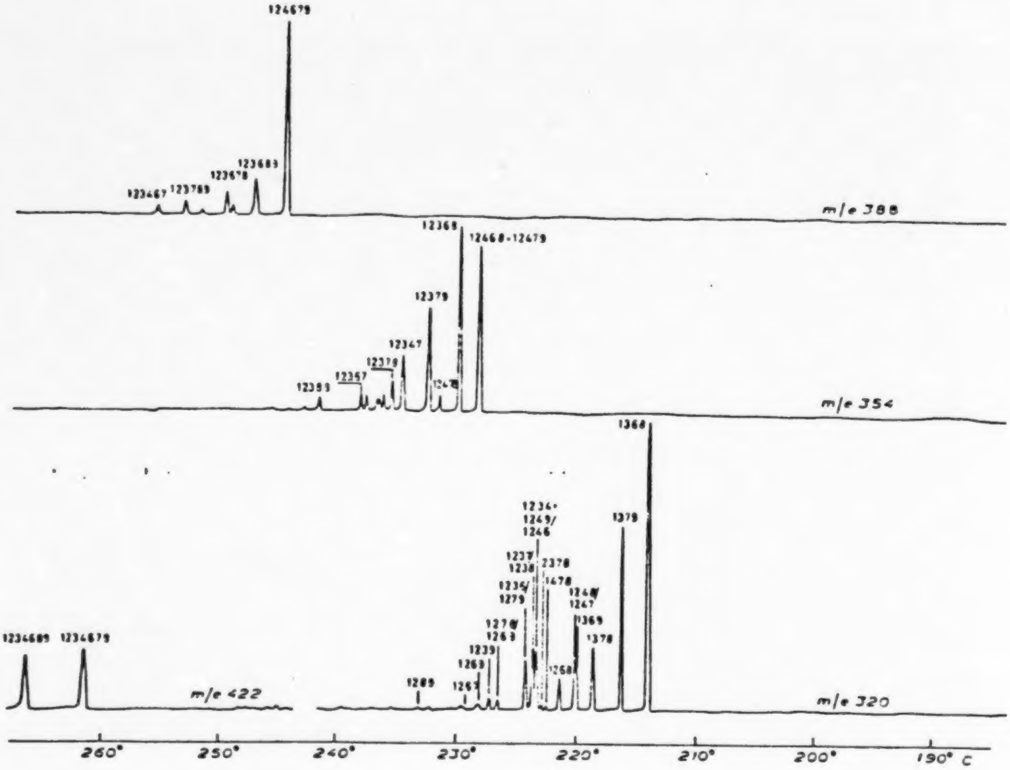

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Figure C-31. Laboratory C mass fragmentogram of tetra-, penta-, hexa- and hepta-CDDS from a flyash sample.

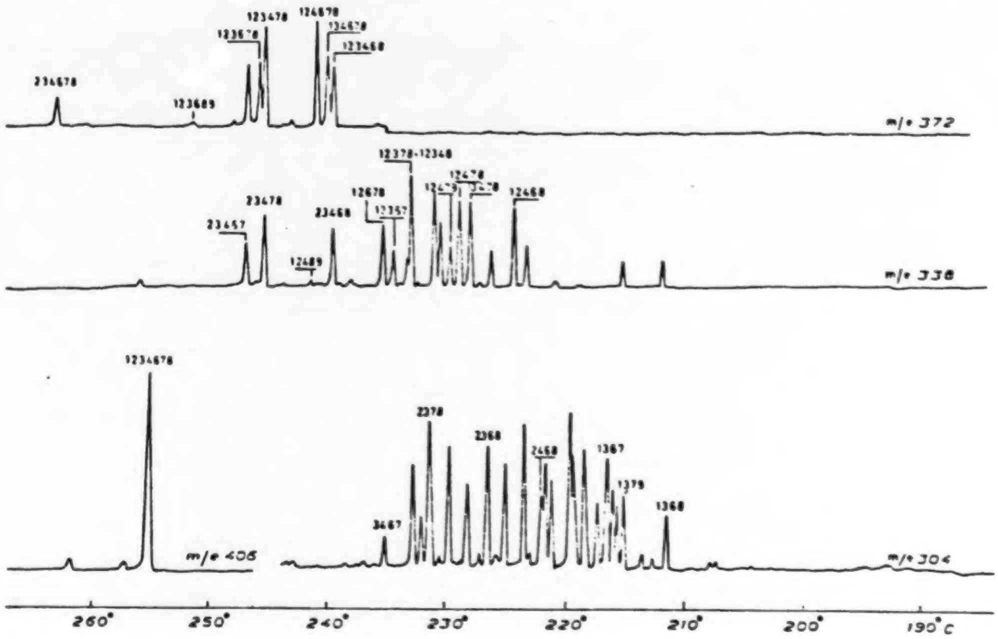
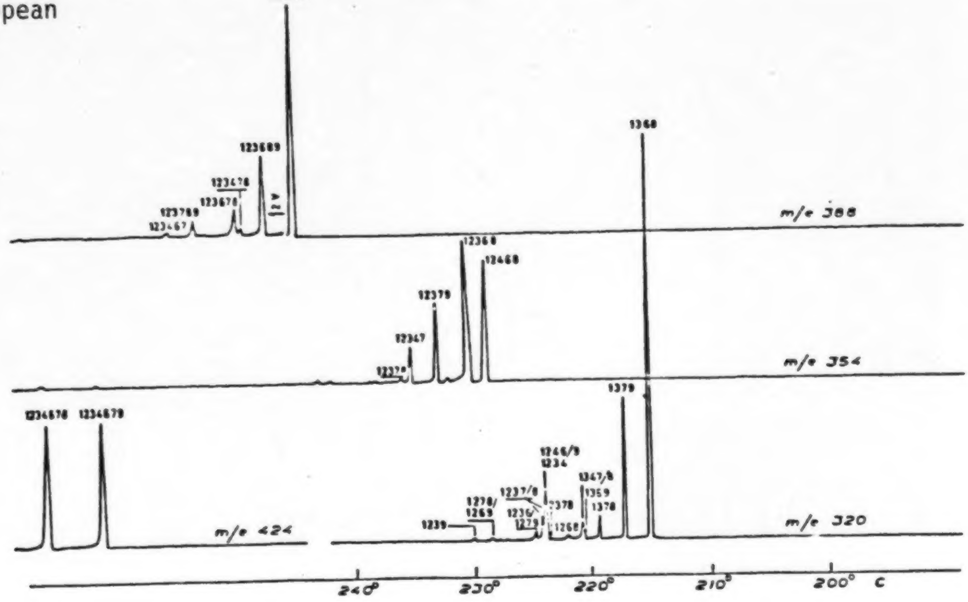


Figure C-32. Laboratory C mass fragmentogram of tetra-, penta-, hexa- and hepta-CDFS from a flyash sample.

Typical
European
Ash



Plant C
Ash

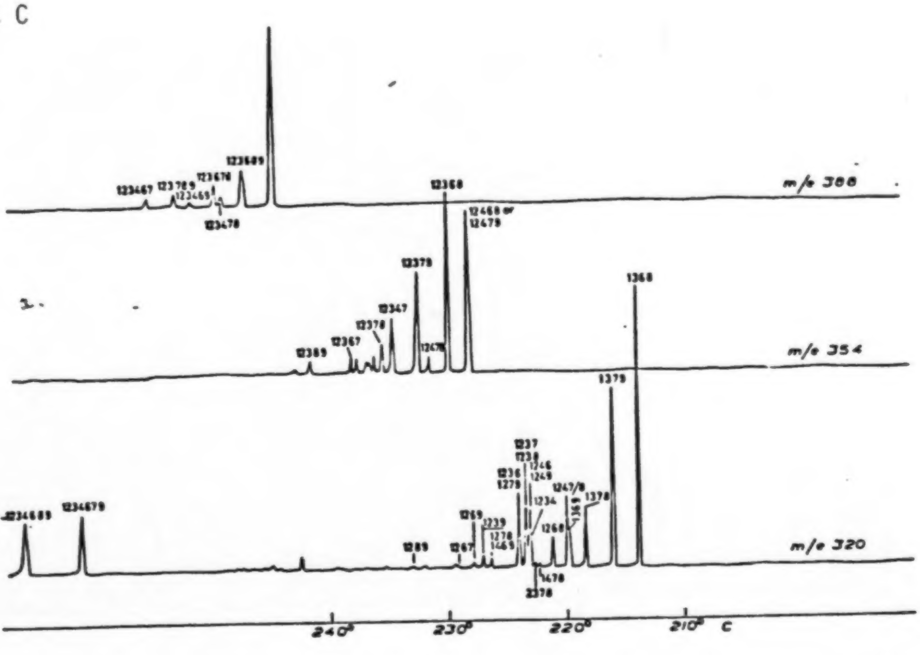


Figure C-33. Comparison of PCDD in Plant C ash and typical European incinerator ash.

European Ash

Plant C Ash

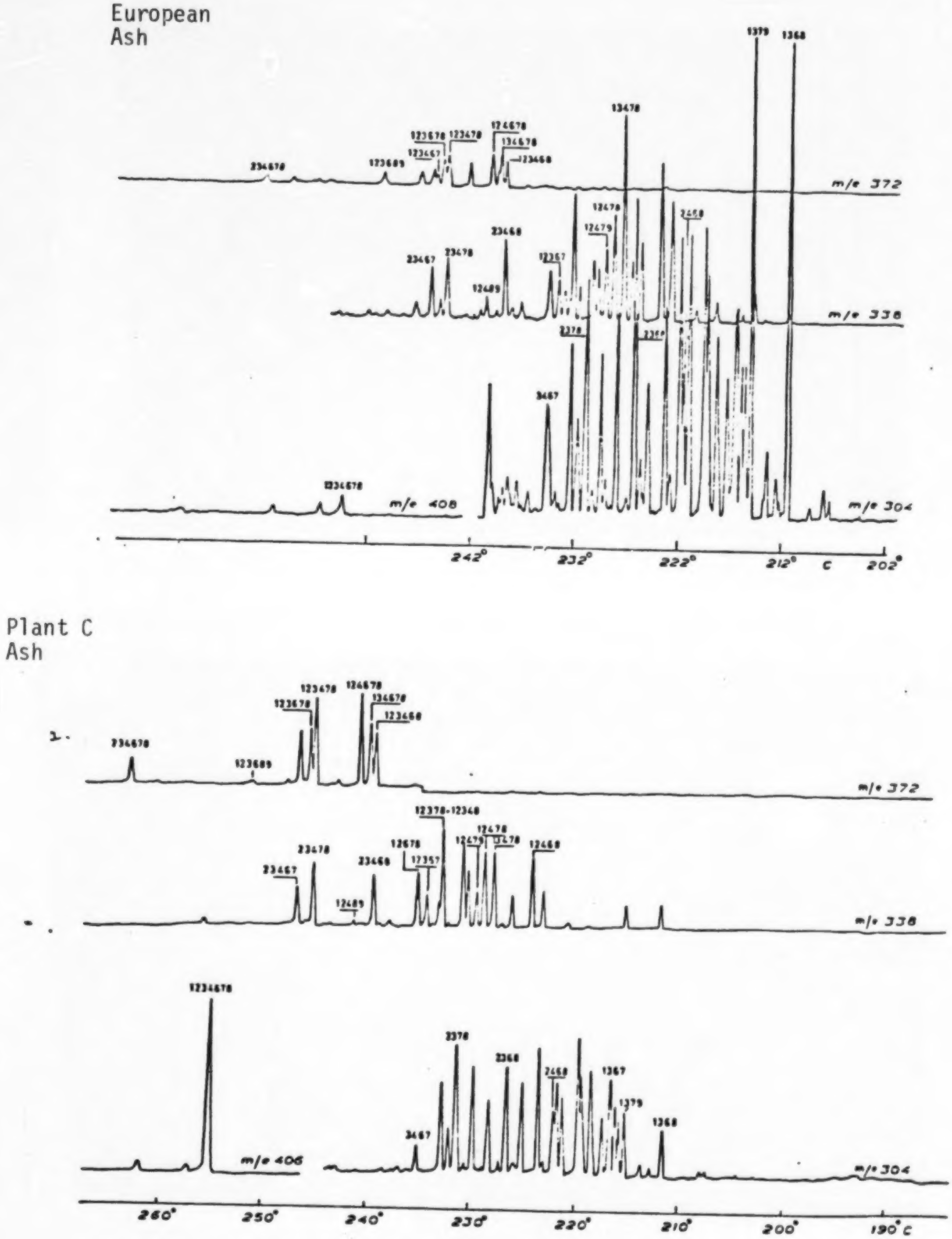


Figure C-34. Comparison of PCDFs in Plant C ash and typical European incinerator ash.